### RICE UNIVERSITY Laser-Induced Graphene for Energy application

By

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#### ABSTRACT

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#### **Muqing Ren**

The rapidly increasing demand for clean energy has stimulated extensive research efforts on the renewable energy technologies, such as fuel cells, hydrogen and oxygen production from water splitting, and rechargeable metal-air batteries. The underlying chemical processes, including the oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), generally suffer from sluggish reaction kinetics. Therefore, effective catalysts are necessary to facilitate the reactions. This thesis focuses on the development of laser-induced graphene (LIG) derived materials and catalysts for electrochemical energy storage devices. LIG is a 3D porous graphene material grown on a flexible substrate that is prepared by a one-step laser scribing process on commercial polyimide (PI) film. The LIG derived from PI is highly porous and is easily synthesized under ambient conditions in a scalable process.

Chapter 1 discusses the oxidation of LIG by O<sub>2</sub> plasma to form oxidized LIG, which boosts its performance in both OER and ORR resulting in an enhanced activity towards rechargeable Li-O<sub>2</sub> battery. In Chapter 2, a distinctive re-lasing method was proposed to prepare metal oxide/LIG composites as efficient catalysts for water oxidation (OER). Unlike the conventional methods, such as solvo-/hydro-thermal, thermal pyrolysis or chemical vapor deposition processes, the re-lasing synthesizes the NiFe-based catalysts through a facile laser scribing process without any tedious procedures. Chapter 3 introduces a bifunctional catalyst Co<sub>3</sub>O<sub>4</sub>/LIG that was synthesized through a facile re-lasing process, showing OER and ORR activity comparable to noble metal-based catalysts in alkaline electrolyte. Furthermore, the Co<sub>3</sub>O<sub>4</sub>/LIG exhibited promising performance in Zn-air and Li-O<sub>2</sub> batteries. Chapter 4 discusses ternary metal oxide/graphene hybrid catalysts by combining ORR-active Co/Mn with OER-active Ni and Fe species to promote the bifunctional activity all in an in situ formed LIG flexible film. These hybrid catalysts exhibit high catalytic activity and surpass the performance of precious metal Pt and RuO<sub>2</sub> catalysts in Znair batteries and demonstrate applications in flexible Zn-air batteries that would be beneficial for wearable and flexible electronic devices. Chapter 5 discusses the performance of bifunctional OER/ORR catalysts MnNiFe/LIG (M111/LIG and M311/LIG, where the numbers reflect the relative molar ratio of Mn, Ni and Fe species) in Li-O<sub>2</sub> and Li-air batteries without the presence of a redox mediator. The underlying mechanism in Li-O<sub>2</sub> battery was investigated. Chapter 6 introduces the design of dual polymer gel electrolyte (DPGE). The combination of DPGE with a Mnbased catalyst enhance the performance of quasi-solid-state Li-O<sub>2</sub> batteries.

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# Nomenclature

PI	Polyimide
BET	Brunauer-Emmett-Teller measurement
CVD	chemical vapor deposition
CV	cyclic voltammetry
DI water	deionized water
DFT	density functional theory
EASA	electrochemically active surface area
EDLC	electric double layer capacitance
EIS	electrochemical impedance spectroscopy
GO	graphene oxide
HER	hydrogen evolution reaction
ICP-OES	inductively coupled plasma optical emission
	spectrometry
LSV	linear sweep voltammetry
ORR	oxygen reduction reaction
OER	oxygen evolution reaction
PANI	polyaniline
PI	polyimide
PVA	poly(vinyl alcohol)
RHE	reversible hydrogen electrode
RDE	rotating-disk electrode

RRDE	rotating ring-disk electrode
RDS	rate-determining step
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TOF	turnover frequency
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
STEM	Scanning transmission electron microscope

### Chapter 1

# Oxidized Laser-Induced Graphene for Efficient Oxygen Electrocatalysis

This chapter was entirely copied from reference 1.

#### **1.1. Introduction**

The ever-increasing demand for clean energy has led to extensive research on the development of renewable energy technologies,<sup>2-4</sup> such as fuel cells,<sup>5, 6</sup> hydrogen and oxygen production from water splitting,<sup>7-9</sup> and rechargeable metal-air batteries.<sup>10, 11</sup> The underlying chemical processes, including the oxygen evolution reaction (OER), hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), generally suffer from slow kinetics.<sup>12</sup> Effective catalysts are necessary to accelerate the reactions. Noble metals and metal oxides, such as Pt, RuO<sub>2</sub> and IrO<sub>2</sub>

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are known to be very efficient.<sup>13-15</sup> However, the high cost and scarcity of the raw materials for these catalysts have slowed their mass production and commercialization. The design and synthesis of efficient noble metal-free catalysts remain a challenge.<sup>16</sup> Recently, carbon nanomaterials doped with heteroatoms such as B, N, P, and S have attracted extensive attention due to their excellent electrocatalytic performance for OER and ORR.<sup>17-22</sup> The modified electroneutrality and charge modulation induced by heteroatoms have led to enhanced electrocatalytic activity.<sup>23, 24</sup> For example, Qu et al. prepared nitrogen-doped graphene by chemical vapor deposition (CVD) that shows excellent ORR activity.<sup>25</sup> Hu et al. demonstrated ORR, OER and HER activity from N and S co-doped graphitic sheets.<sup>26</sup> Lu et al. reported the enhanced OER performance from multiwall carbon surface oxidation, hydrothermal nanotubes treated by annealing and electrochemical activation.<sup>27</sup> Although the metal-free catalysts have proven to be promising candidates for electrocatalysis, the complicated and multi-step synthetic process requiring CVD and hydrothermal reactions is a disadvantage for large-scale applications. The facile synthesis of catalysts with excellent electrocatalytic performance and understandable mechanistic behaviors remain of interest.

We present here an efficient metal-free catalyst for OER/ORR based on oxidized laser-induced graphene (LIG-O). LIG is a 3D porous graphene material fused to a flexible substrate that is prepared by a one-step laser scribing process on commercial polyimide (PI, Kapton®) film.<sup>28-30</sup> LIG derived from PI is highly porous and is easily formed in the air at room temperature in a scalable process. The oxidation of LIG by an O<sub>2</sub> plasma to form LIG-O boosted its OER performance, exhibiting a low onset potential of 260 mV with a low Tafel slope of 49 mV dec<sup>-1</sup>, as well as an increased activity for ORR. Additionally, LIG-O showed unexpectedly high activity in catalyzing Li<sub>2</sub>O<sub>2</sub> decomposition in Li-O<sub>2</sub> batteries. The overpotential upon charging was decreased from 1.01 V in LIG to 0.63 V in LIG-O. The oxygen-containing groups make essential contributions, not only by providing the active sites, but also by facilitating the adsorption of OER intermediates and lowering the activation energy. LIG-O and other oxidized graphitic nanomaterials may be promising catalysts for various energy related applications.

### 1.2. Oxidized Laser-Induced Graphene for Efficient Oxygen Electrocatalysis

#### **1.2.1. Experimental Section**

#### 1.2.1.1. Material Synthesis

**Preparation of laser-induced graphene (LIG).** All samples were prepared under room temperature and ambient air. Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser cutter system (10.6 μm, Universal XLS10MWH laser cutter platform) on the Kapton<sup>®</sup> polyimide film in air using 3% of full power and 5% of full speed with an image density of 6.

**Preparation of oxidized laser-induced graphene (LIG-O).** The incorporation of oxygen functional groups to LIG was performed using a Model

1020 Plasma Cleaner (Fischione Instruments). Briefly, the as-prepared LIG on PI was placed in the plasma cleaner chamber and the oxidation was performed in the O<sub>2</sub> environment for 10 min. Then the LIG-O was scratched from the PI for further testing.

**Preparation of thermally annealed (LIG-A).** ~10 mg LIG was thermally reduced at 750 °C for 2 h in an Ar atmosphere at a ramping rate of 5 °C min<sup>-1</sup>. The thermal reduction removed most of the oxygen-containing groups on the LIG.

#### 1.2.1.2. Material Characterization

**General characterization.** SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images were obtained by a JEOL 2100F field emission gun transmission electron microscope. XPS was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was carried using a Perkin Elmer Optima 8300 instrument. The BET characterization was done by a Quantachrome Autosorb-3b BET surface analyzer.

**Electrochemical measurements.** For preparation of the working electrode, 4 mg of the catalyst and  $80 \,\mu\text{L}$  of  $5 \,\text{wt\%}$  Nafion solution were mixed in 1 mL water/ethanol (1/1, v/v) followed by 2 h bath-sonication (Cole Parmer, model 08849–00) to form a homogeneous ink. 8  $\mu$ L of the ink was loaded onto a rotating disk electrode (RDE, glassy carbon, 5 mm in diameter), and dried in air at room temperature. RuO<sub>2</sub> (Aldrich Chemical Company, Inc.) working electrode was prepared by the same procedures for comparison. The electrochemical measurements were carried out in a 3-electrode configuration using a CHI 608D electrochemical workstation. A Pt plate and Hg/HgO (1 M KOH) were used as the counter and reference electrode, respectively. The tests regarding oxygen evolution were done on the RDE at 1600 rpm in 1 M KOH with 95% iR compensation unless otherwise noted. 95% instead of 100% iR compensation was applied to avoid the possible over-compensated resistance during the test, because the equivalent serial resistance might be affected by bubble generation/desorption, turbulence and the local change of pH at high current density. The potential was normalized with RHE. The tests regarding oxygen reduction were done in 0.1 M KOH with 95% iR compensation. O<sub>2</sub> bubbling in the electrolyte was maintained throughout the measurement to ensure the continuous saturation of O<sub>2</sub>.

For the OER test at different temperatures, a Ag/AgCl electrode (with saturated potassium chloride electrolyte) was used as the reference electrode. The test was carried out using RDE at 1600 rpm in 1 M KOH. The effects of temperature on pH and the potential of Ag/AgCl were corrected.

The number of electrons transferred (n) during ORR was calculated by Koutecký-Levich (K-L) equation based on the LSV curves with varying rotating speed from 225 to 1600 rpm. According to Equation 1.1, at various electrode potentials:

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$$\frac{1}{j} = \frac{1}{j_{\rm K}} + \frac{1}{j_{\rm L}} = \frac{1}{j_{\rm K}} + \frac{1}{B\omega^{1/2}}$$
$$B = 0.2nFC_0 D_0^{2/3} \nu^{-1/6}$$

#### **Equation 1.1. Koutecký–Levich equation.**

where *j* is the measured current density, and  $j_{\rm K}$  and  $j_{\rm L}$  are the kinetic and diffusion-limiting current densities, respectively.  $\omega$  is the rotating speed in rpm, *F* is the Faraday constant (96485 C mol<sup>-1</sup>), *C*<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>), *D*<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH (1.9 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>), and *v* is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

Rotating ring-disk electrode (RRDE) measurement. The catalyst inks and electrodes were prepared by the same method as those of RDE. We combined a CHI 608D workstation (CH Instruments, Inc.) with a CV-50W Voltammetric Analyzer (Artisan) to carry out the measurement. The disk electrode was scanned at a rate of 20 mV s<sup>-1</sup> and the ring potential was kept constant at 0.4 V vs. Ag/AgCl. The HO<sub>2</sub><sup>-</sup> yield and n were calculated using **Equation 1.2** and **Equation 1.3**:

$$HO_2^-\% = 200\% \times \frac{I_r/N}{I_r/N + I_d}$$

#### Equation 1.2. Calculation of the HO<sub>2</sub>-% from the RRDE measurement.

$$n = 4 \times \frac{I_{\rm d}}{I_{\rm r}/{\rm N} + I_{\rm d}}$$

#### Equation 1.3. Calculation of *n* from the RRDE measurement.

where  $I_d$  is disk current,  $I_r$  is ring current and N is collection efficiency (0.38).

#### 1.2.1.3. DFT Calculation

The structural optimizations were carried out by adopting the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional, along with the projector-augmented wave (PAW) potentials. The electronic wave functions were expanded in a plane wave basis set with the kinetic energy cutoff of 400 eV. For the Brillouin zone integration,  $2 \times 1 \times 1$  Monkhorst-Pack k-point meshes were used. The energy convergence criterion for the electronic wavefunction was set to be  $10^{-5}$  eV. A vacuum distance of about 10 Å was chosen to guarantee a negligible spurious interaction between layers.

As has been proposed,<sup>31, 32</sup> the free energy of O<sub>2</sub> is derived as  $G(O_2) = 2G(H_2O) - 2G(H_2) + 4.92 \text{ eV}$ , where 4.92 eV is taken from the free energy change of reaction O<sub>2</sub> + 2H<sub>2</sub>  $\rightarrow$  2H<sub>2</sub>O under the standard condition. The free energy of OH<sup>-</sup> is determined as  $G(OH^-) = G(H_2O) - G(H^+)$  assuming H<sup>+</sup> + OH<sup>-</sup>  $\rightarrow$  H<sub>2</sub>O is in equilibrium. The free energy of H<sup>+</sup>,  $G(H^+)$ , is that of half of hydrogen molecule,  $1/2G(H_2)$ . At a pH different from 0,  $G(H^+)$  is corrected by the concentration dependence of the entropy,  $G(pH) = kTln[H^+] = -kTln10 \times pH$ . The effect of the bias is included for all states involving electrons in the electrode, by shifting the energy of this state by *-neU*, where *n* and *U* are the number of electrons involved and the electrode potential, respectively. Under these approximations, the maximum potential achieved by thermodynamics is ~0.4 eV at pH = 14, which is consistent with the standard

reduction potential of the OER in alkaline solution. The Gibbs free energies of intermediates at U = 0 V is determined as  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ , where  $\Delta E$ ,  $\Delta ZPE$  and  $\Delta S$  are the difference in total DFT energies, zero-point energies due to reactions, and the change of the entropy.  $\Delta E$  are taken from DFT calculations,  $\Delta ZPE$  and  $\Delta S$  are taken from references.<sup>31, 32</sup>

# 1.2.1.4. Electrochemically active surface area and electrochemical impedance spectroscopy

The electrochemically active surface area (EASA) is calculated from the double-layer capacitance of the catalyst.<sup>33</sup> Typically, the CV curves of LIG catalysts were recorded in non-Faradic region (-0.05 to 0.05 V *vs* Hg/HgO in 1 M KOH) at scan rates ranging from 10 to 100 mV s<sup>-1</sup>. The current density *j* solely originated from the charging/discharging of the double layer capacitance as given by:

$$j = C_{\rm dl} \cdot \frac{dV}{dt}$$

#### Equation 1.4. Calculation of the *C*<sub>dl</sub> of LIG-based catalysts.

$$EASA = \frac{C_{dl}}{C_s}$$

#### Equation 1.5. Calculation of the EASA of LIG-based catalysts.

where  $C_s$  is the ideal specific capacitance of a smooth planar surface. The value of  $C_s$  is determined to be 40  $\mu$ F cm<sup>-2</sup> according to a recent study, where the  $C_s$ 

values on a variety of electrodes have been evaluated in 1 M OH<sup>-.33</sup> 40  $\mu$ F cm<sup>-2</sup> is a creditable value according to the results from a variety of electrode surfaces.<sup>33</sup> The geometric surface area (GSA) of the glassy carbon electrode is 0.196 cm<sup>2</sup>. The *j* is recorded at 0 V (*vs* Hg/HgO).

The electrochemical impedance spectroscopy (EIS) measurements were performed by a CHI 608D electrochemical workstation. EIS spectra were collected by applying ac potentials covering the frequency range from 100000 to 0.1 Hz with an amplitude of 5 mV. Nyquist plots were used to study the surface intermediates coverage and charge transfer properties of the electrodes. The equivalent circuit used to simulate the electrochemical process is shown in **Figure 1.1**:<sup>34</sup>



Figure 1.1 Equivalent circuit for the EIS analysis of LIG-based catalysts.

 $R_{\rm s}$  is the equivalent series resistance and  $C_{\rm dl}$  is double-layer capacitance.  $R_1$  +  $R_2$  represents the charge transfer resistance.  $C_{\rm ads}$  is the capacitance associated with the intermediate adsorbed on the electrode during oxygen evolution. The relation between  $C_{\rm ads}$  and the surface coverage ( $\theta$ ) of intermediate at a potential is defined as in Equation 1.6.<sup>35</sup>

$$C_{\rm ads}(E) = \sigma \; \frac{{\rm d}\theta(E)}{{\rm d}E}$$

#### **Equation 1.6. Determination of the** *C*<sub>ads</sub>.

 $\sigma$  is the charge density for a monolayer coverage and is assumed to be constant.  $C_{ads}$  is obtained from the EIS and normalized by EASA. The surface coverage is estimated by integrating  $C_{ads}$  with *E*, and normalized at a potential below OER onset (1.21 V *vs* RHE).

#### 1.2.1.5. Identification of the OER rate determining step (RDS)

The OER mechanistic pathways on carbon-based catalysts are generally considered as in the following **Equation 1.7**.<sup>36</sup>

 $M + OH^{-} \rightarrow M - OH^{*} + e^{-} \cdots (a)$   $M - OH^{*} + OH^{-} \rightarrow M - O^{*} + e^{-} \cdots (b)$   $M - O^{*} + OH^{-} \rightarrow M - OOH^{*} + e^{-} \cdots (c)$   $M - OOH^{*} + OH^{-} \rightarrow M + H_{2}O + O_{2} + e^{-} \cdots (d)$ 

#### **Equation 1.7. Proposed OER mechanistic pathways.**

M is a catalytically active surface site, and the superscript \* means it is a surface state.

Since the LSV curves were recorded at a very low scan rate, only the RDS would be irreversible while all other elementary steps were in quasi-equilibrium. The total anodic current is limited by the RDS and expressed by Equation 1.8.<sup>37</sup>

$$i = i_0 e^{\frac{\alpha_a F \eta}{RT}}$$

#### Equation 1.8. Effect of overpotential on the anodic current.

where  $i_0$  is the exchange current,  $\alpha_a$  is the transfer coefficient, F is Faraday's constant and  $\eta$  is the overpotential. Then the Tafel slope *b* is determined by Equation 1.9.

$$b = \frac{\partial \eta}{\partial \log i} = 2.303 \frac{RT}{\alpha_{\rm a} F}$$

#### Equation 1.9. Relationship between Tafel slope and transfer coefficient.

For a multistep reaction that has one RDS, the  $\alpha_a$  can be estimated by **Equation 1.10**.<sup>37</sup>

$$\alpha_a = \frac{n_{\rm f}}{\nu} + n_r \beta$$

#### **Equation 1.10. Estimation of the transfer coefficient in OER.**

where  $n_f$  is the number of electrons transferred before RDS,  $\nu$  is the number of times that RDS occurs,  $n_r$  is the number of electrons transferred in RDS.  $\beta$  is the symmetry factor, and indicates how the changes in overpotential will affect the changes in the activation energy.  $\beta$  is generally assumed to be 0.5.<sup>38</sup>

For a preliminary estimation, if Equation 1.7a is the RDS,  $n_f$  is 0,  $n_r$  is 1 and  $\alpha_a$  is 0.5. The Tafel slope *b* would be ~120 mV dec<sup>-1</sup>. If Equation 1.7b is the RDS,  $n_f$  is 1, v is 1,  $n_r$  is 1 and  $\alpha_a$  is 1.5. The Tafel slope *b* would be ~40 mV dec<sup>-1</sup>. Hence, based on the electrochemiucal data (see below), for LIG-0, Equation 1.7b is the RDS. For LIG-A, **Equation 1.7**a is the RDS.

The surface coverage  $\theta$  is further included to study the reaction mechanism.<sup>34, 35</sup> For LIG-A, **Equation 1.7**a is the RDS and thus the current is related to the velocity  $\upsilon$  of the RDS as shown by Equation 1.11:<sup>38</sup>

$$i \propto v = k_1 \cdot \theta_{\rm M} \cdot a_{\rm OH^-} \cdot e^{\frac{\beta FE}{RT}}$$

#### Equation 1.11. Effect of overpotential on the anodic current of LIG-A.

 $k_1$  is forward rate constant and *E* is the applied potential.  $\theta_M$  is the proportion of surface sites exist as M. Its value ranges from 0 to 1, suggesting no M or all the sites exist as M. It is not applicable to normalize the surface coverage  $\theta$  to unity. But it is reasonable that  $\theta$  will increase as the potential increases. For LIG-A at low overpotential ( $\eta$  = 300-400 mV) where the OER starts to happen,  $\theta_M$  is close to 1. Hence, the Tafel slope is shown as **Equation 1.12**:

$$b_{\text{LIG}-A} = \frac{\partial \eta}{\partial \log i} = \frac{\partial E}{\partial \log \upsilon} = 2.303 \frac{RT}{\beta F} = \sim 120 \text{ mV dec}^{-1}$$
13

Equation 1.12. Estimation of the Tafel slope for LIG-A.

The observed *b* of LIG-A is 117 mV dec<sup>-1</sup> (see below) that agrees with the analysis.<sup>38</sup>

For LIG-O, **Equation 1.7**b is the RDS and the current is related to the velocity of the RDS in **Equation 1.13**:<sup>38</sup>

$$i \propto \upsilon = \theta_{\rm M-OH} \cdot a_{\rm OH^-} \cdot e^{\frac{\beta FE}{RT}}$$

Equation 1.13. Effect of overpotential on the anodic current of LIG-O.

In this case, **Equation 1.7**a is in equilibrium as show as **Equation 1.14**:

$$k_1 \cdot \theta_{\mathrm{M}} \cdot a_{\mathrm{OH}^-} \cdot e^{\frac{\beta FE}{RT}} = k_{-1} \cdot \theta_{\mathrm{M}-\mathrm{OH}} \cdot e^{\frac{(\beta-1)FE}{RT}}$$

Equation 1.14. OER equilibrium reaction of LIG-O.

Therefore:

$$\upsilon = \theta_{\mathrm{M-OH}} \cdot a_{\mathrm{OH}^{-}} \cdot e^{\frac{\beta FE}{RT}} = \theta_{\mathrm{M}} \cdot \frac{k_{1}}{k_{-1}} \cdot a_{\mathrm{OH}^{-}}^{2} \cdot e^{\frac{(\beta+1)FE}{RT}}$$

### Equation 1.15. Estimation of the reaction velocity for LIG-O.

And the Tafel slope is shown as **Equation 1.16**:

$$b_{\text{LIG-O}} = \frac{\partial E}{\partial \log \upsilon} = 2.303 \frac{RT}{(\beta + 1)F} = \sim 40 \text{ mV dec}^{-1}$$

#### Equation 1.16. Estimation of the Tafel slope for LIG-O.

It should be noted that, as the overpotential is increased, the  $\Delta G$  of **Equation 1.7**a will be further lower (more negative) and the formation of M-OH<sup>\*</sup> is preferred at high overpotential. As a result, at higher overpotential  $\theta_{M-OH}$  will be close to 1, and the Tafel slope is shown as **Equation 1.17**:

$$b = \frac{\partial E}{\partial \log \upsilon} = 2.303 \frac{RT}{\beta F} = \sim 120 \text{ mV dec}^{-1}$$

#### Equation 1.17. Estimation of the Tafel slope for LIG-O at high overpotential.

The experimental data (see below) shows the two Tafel regions with *b* of 49 and 134 mV dec<sup>-1</sup>, demonstrating the proposed mechanism of LIG-O. It should be noted that in practical measurements (especially at high overpotential), experimental factors such as mass transport limitations, charge transfer efficiency, side reactions at high potential etc. will have interference on the Tafel plots, and lead to a much higher *b*.

Our analysis has shown the two distinct RDS of LIG-O and LIG-A based on the surface coverage  $\theta$  and overpotential  $\eta$ . The RDS of LIG-A is the formation of discrete adsorbed hydroxide intermediates which may be ascribed to the low content of oxygen-containing groups. The RDS of LIG-O is the formation of epoxide

on the surface of LIG. The low affinity (compared with transition metal oxides) may be rate-determining.

#### 1.2.1.6. Li-O<sub>2</sub> battery using LIG as the air cathode

Briefly, a piece of LIG-O film was carefully scraped from the PI substrate and used as the air cathode without any binders or catalysts. The cells were assembled in an argon-filled glovebox with a lithium metal anode. The separator was Celgard 2400 membrane. A stainless-steel mesh was used as the supporter and current collector for the LIG-O film to allow O<sub>2</sub> diffusion. The electrolyte was 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) with 0.05 M LiI in tetraethylene glycol dimethyl ether (TEGDME).<sup>39</sup> The total area of the cathode that exposed to O<sub>2</sub> was 12.5 mm<sup>2</sup> (0.063 mg of LIG-O). Li-O<sub>2</sub> batteries with commercially available Pt/C (Sigma-aldrich, 205931) as the cathode catalysts were fabricated for comparison. Then the cells were rested at open circuit condition with O<sub>2</sub> purging for 10 h prior to test. For the galvanostatic charge/discharge measurements, the current was kept constant at 0.01 mA and the time was limited to 6h. The lower and upper voltage limits were 2.5 and 4.3 V (*vs* Li), respectively.

#### 1.2.2. Result and Discussion

As depicted in **Figure 1.2a**, the LIG-O was prepared by direct laser scribing on Kapton<sup>®</sup> PI films followed by O<sub>2</sub> plasma treatment, which is known to create surface defects and oxygen-containing groups on carbon materials.<sup>40</sup> According to previous work on graphene, the LIG powder (removed from the PI substrate) was heated at 750 °C in Ar for 2 h to remove most of the surface oxygen-containing groups to produce annealed LIG (LIG-A).<sup>41, 42</sup> The highly porous filiform structure of LIG was maintained in LIG-O after the O<sub>2</sub> plasma treatment as shown in the scanning electron microscope (SEM) images in Figure 1.2b, Figure 1.3 and Figure 1.4. However, this structure collapsed slightly after thermal annealing and resulted in the flake-like structure of LIG-A as shown in **Figure 1.5.** The typical multilayer graphitic structure of LIG remained after either treatment, as revealed by the transmission electron microscopy (TEM) images in Figure 1.2, Figure 1.6 and Figure 1.7, which is consistent with the clearly identified D, G and 2D peaks in the Raman spectra (Figure 1.8).<sup>28</sup> LIG-O has abundant graphene edge structures that improve the electrolyte wettability and retain good electric conductivity. The  $I_D/I_G$ increased after the treatments, indicating that more defects were formed.<sup>43</sup> Oxygen plasma treatment also increased the porosity of LIG. The Brunauer-Emmett-Teller (BET) surface area of LIG-O is 246.8 m<sup>2</sup> g<sup>-1</sup>, whereas that of LIG is 178.7 m<sup>2</sup> g<sup>-1</sup> (Figure 1.8).



Figure 1.2 Preparation and structural characterization of LIG-O.

(a) Preparation of LIG-O. (b) SEM and (c) TEM images of LIG-O.



Figure 1.3 SEM images of LIG-O.



Figure 1.4 SEM images of LIG.



Figure 1.5 SEM images of LIG-A.



Figure 1.6 TEM images of LIG-O.



Figure 1.7 TEM images of LIG-A.



Figure 1.8. Raman spectra and BET messurement.

(a) Raman spectra of LIG-O, LIG and LIG-A. (b) The ratio between the intensities of D and G band in (a). And nitrogen adsorption/desorption plot of (c) LIG and (d) LIG-O.

The OER activities of LIG-O, LIG and LIG-A were characterized in 1 KOH by using a rotating disk electrode (RDE, glassy carbon (GC)) loaded with the catalyst ink at 1600 rpm, with a Pt counter electrode and a Hg/HgO reference electrode. The use of RDE was to ensure electrolyte mixing and fast removal of bubbles generated at the catalyst surface. As shown by the linear sweep voltammetry (LSV) results in **Figure 1.9**a, LIG was moderately active for OER while LIG-O showed a remarkably lowered onset potential of 260 mV with enhanced current density (*j*<sub>GSA</sub>, current normalized by the geometric surface area of the electrode). The  $i_{GSA}$  of LIG-O reached 10 mA cm<sup>-2</sup> at a low overpotential of 364 mV; such a low value is comparable to that of transition metal-based catalysts.<sup>33, 44-47</sup> Figure 1.9b shows the Tafel plots derived from the LSV curves. The Tafel slope of LIG-0 is 49 mV dec<sup>-1</sup>, which is lower than most metal-free catalysts (Table 1.1), demonstrating the significantly enhanced OER activity after O<sub>2</sub> plasma treatment. LIG-A has a performance inferior to LIG-O and LIG, with an onset potential of 290 mV and a Tafel slope of 117 mV dec<sup>-1</sup>. Although the benchmark RuO<sub>2</sub> has the lowest onset potential of 210 mV, the higher Tafel slope of 67 mV dec<sup>-1</sup> made its performance less competitive with LIG-O at high current density. The Tafel slope of RuO<sub>2</sub> ranges from  $\sim$ 50 to  $\sim$ 100 mV dec<sup>-1</sup> in the literature, probably due to the structurally sensitive activity on RuO<sub>2</sub> in that the Tafel slope depends on the orientation of the lattice.<sup>44,45</sup> LIG-O also showed impressive OER activity in 0.1 M KOH (Figure 1.10). The onset potential was 290 mV with a Tafel slope of 56 mV dec<sup>-1</sup> and the overall performance surpassed that of RuO<sub>2</sub>.



Figure 1.9 OER performance characterized in 1 M KOH.

(a) LSV curves of LIG-O, LIG, LIG-A and a GC electrode recorded in 1 M KOH at a scan rate of 2 mV s<sup>-1</sup>. (b) Tafel plots calculated from (a). (c) LSV curves with current normalized by the EASA. (d) Stability test. Potential profile of LIG-O for bulk OER at 5 mA cm<sup>-2</sup>.

Catalyst	Electrolyte	Onset potential (V)	Tafel Slope (mV dec <sup>-1</sup> )
	1 M KOH	1.49	49
LIG-0	0.1 M KOH	1.52	56
N, O, P tri-doped porous carbon <sup>48</sup>	1 М КОН	1.52	84
O-CNTs <sup>19</sup>	1 М КОН	1.52	47.7
Pristine CNTs <sup>49</sup>	1 М КОН	1.58	60
B doped CNTs <sup>50</sup>	1 M KOH	1.65	/
NG-CNT <sup>51</sup>	0.1 M KOH	1.54	141
N, S co-doped graphitic sheets <sup>26</sup>	0.1 M KOH	1.49	71
N, S co-doped Graphene <sup>52</sup>	0.1 М КОН	1.52	59
Oxidized carbon cloth <sup>53</sup>	0.1 М КОН	1.56	82
O-Graphene Foam <sup>54</sup>	0.1 М КОН	1.57	137

Table 1.1. Comparison of OER performance of LIG-O with recently reportedmetal-free OER catalysts.



Figure 1.10 OER performance of LIG-O in 0.1 M KOH.

(a) LSV curves of LIG-O recorded in 0.1 M KOH at a scan rate of 2 mV s<sup>-1</sup> and (b) the corresponding Tafel plots. Inset in (a) shows the potential profile of OER at 2 mA cm<sup>-2</sup>.

The OER activities were further studied based on the electrochemically active surface area (EASA) that was calculated from the double-layer capacitance recorded in the non-Faradic region (Experimental Section and **Figure 1.11**).<sup>33</sup> LIG-O has the highest EASA of 83.6 cm<sup>2</sup> per geometric cm<sup>2</sup> of the GC electrode. The values of LIG and LIG-A are 36.3 and 33.0 cm<sup>2</sup>, respectively. The high EASA of LIG-O indicates its porous structure and good compatibility with the electrolyte. It should be noted that the increased hydrophilicity after oxidation may have also contributed to the high EASA. As shown in **Figure 1.9**c, LIG-O has a much higher *j*<sub>EASA</sub> than that of LIG and LIG-A, indicating that the oxidation not only increased the EASA of LIG, but also created more active sites; both contributed to the high activity. At 350 mV

overpotential, the *j*<sub>EASA</sub> of LIG-O is as high as 0.08 mA cm<sup>-2</sup>; this value is higher than that of transition metal based catalysts.<sup>27</sup> Additionally, the long-term stability of LIG-O is outstanding as shown in **Figure 1.9**d. After bulk OER at 5 mA cm<sup>-2</sup> for 20000 s, the overpotential slightly increased by 13 mV, suggesting a negligible degradation of the catalysts.



Figure 1.11. Determination of the *C*<sub>dl</sub> and EASA.

CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s<sup>-1</sup> for (a) LIG-O, (c) LIG and (e) LIG-A. Current density at 0 V (*vs* Hg/HgO) as a function of scan rate for (b) LIG-O, (d) LIG and (f) LIG-A. The contact angle measurements and wettability of surfaces of (g) LIG and (h) LIG-O on PI substrate.

In order to explain the high OER activity of LIG-O, we first excluded the contamination by metal impurities. The CV curve (**Figure 1.12**) shows no redox peaks in the OER region, indicating that the OER activity was not from any redox mediator (e.g. Ni<sup>2+</sup>  $\rightarrow$  NiOOH). Likewise, no nanoparticles were observed in the TEM images. This is consistent with the high-resolution XPS spectra shown in **Figure 1.13**, where no detectable contamination of Ni, Co or Fe was found (the transition metal oxides are generally considered highly active for OER). Inductively coupled plasma optical emission spectrometry (ICP-OES) confirmed there is no detectable contamination from Co, Ni or Fe species (<0.0005 at%).



Figure 1.12. CV curve of LIG-O in 1 M KOH.



Figure 1.13. XPS spectra of LIG-0.

## (a) XPS survey spectrum of LIG-O. Elemental spectra in (b) Fe 2p, (c) Co 2p and (d) Ni 2p regions.

Detailed investigations of the OER activity of LIG-O were then carried out. **Figure 1.14**a shows the elemental composition of the catalysts as determined by XPS, where LIG-O has a high oxygen content of 11.6 % compared to 3.1 % for LIG and 1.4 % for LIG-A (**Table 1.2**), suggesting the significant effects of oxygencontaining groups on OER activity. High-resolution XPS spectra (**Figure 1.14**b and **Figure 1.14**c, **Figure 1.15** and **Figure 1.16**) further reveal the ratios of the oxygen and carbon species. The O 1s spectra was deconvoluted into three peaks that were assigned to C-O (~533.5 eV), C=O (~532.3 eV) and physisorbed oxygen/carbonate species (~530.5 eV), respectively.<sup>19, 55-60</sup> The C 1s spectra were deconvoluted into the peaks from sp<sup>2</sup> (284.5 eV), sp<sup>3</sup> (285.0 eV), C-O (285.9 eV), C=O (287.2 eV) and O-C=O (288.7 eV).<sup>57, 58</sup> As summarized in **Table 1.3**, LIG-O has the highest C=O content (11.0 % *vs* 4.8 and 0.2 % of LIG and LIG-A, respectively) while its C-O content is comparable to those of LIG and LIG-A. Hence, the OER activity is strongly correlated to the C=O content. Recent studies on carbon nanotubes suggest that the carbon atoms near C=O are the predominantly active sites for OER due to the charge redistribution induced by the highly electronegative oxygen atoms,<sup>19, 27, 60</sup> a conclusion that is supported by the low activity of LIG-A compared to LIG-O.

Catalyst	C (at%)	0 (at%)
LIG-O	88.4	11.6
LIG	96.9	3.1
LIG-A	98.6	1.4

Table 1.2. Elemental composition of LIG-O, LIG and LIG-A from XPS.



Figure 1.14. Analysis on the OER mechanism of LIG-0.

(a) XPS survey spectra of LIG-O, LIG and LIG-A. (b) XPS O 1s and (c) C 1s spectra of LIG-O. (d) Surface coverage of OER intermediates. (e) LSV curves of LIG-O recorded at different temperature and (f) Arrhenius plots fitted at different overpotentials.

Catalyst	sp <sup>2</sup>	sp <sup>3</sup>	C-0	C=0	0-C=0
LIG-O	60.3	20.6	7.0	11.0	3.1
LIG	65.7	24.2	5.3	4.8	<0.1
LIG-A	66.7	28.1	4.1	0.2	<0.1

Table 1.3. XPS fitting results of carbon species on LIG-O, LIG and LIG-A (at%).



Figure 1.15. XPS elemental spectra in C 1s region.



Figure 1.16. XPS elemental spectra in 0 1s region.

First-principles calculations were exploited to understand and quantify the mechanism of OER catalysis at graphene edges.<sup>61, 62</sup> The spin-polarized density functional theory (DFT) calculations were performed using the Vienna *ab-initio* simulation package (VASP)<sup>61, 62</sup> code (Experimental Section). As shown in **Figure 1.17** and **Figure 1.18**, the edge sites on graphene that are adjacent to C=O were taken into consideration to determine the change of Gibbs free energy which represents the thermodynamic barriers during OER. In the 4-electron OER process, the step with maximum Gibbs free energy change ( $\Delta G_{max}$ ) is recognized as the thermodynamics-limiting step as shown in **Figure 1.17**e. The For the oxygen-free edges, the  $\Delta G_{max}$  are higher than 1.27 eV (**Table 1.4**), which indicates a very high overpotential for OER. On the contrary, a low  $\Delta G_{max}$  of 0.49 eV was found for the oxygen-containing edges (hex-O-C). The LIG-O has abundant edges as revealed by the TEM and EASA analyses, and thus has more active sites in good contact with the

electrolyte. The C=O moieties on or near the five/seven-membered rings may also activate their neighboring carbon atoms to have higher OER activity, since the distorted electron clouds around the five/seven-membered rings would be more easily affected. An abundance of five/seven-membered rings are present in LIG since it forms through a rapid cooling in the lasing process, making it kinetic graphene-like. For instance, the  $\Delta G_{max}$  of a pentagonal site is 0.72 eV and thus these sites may be catalyzing OER as the overpotential increases (pen-O-C in **Figure 1.17**). These calculations show that the oxygen-defects may indeed significantly enhance the OER performance of graphene edges by lowering the  $\Delta G_{max}$  on adjacent carbons.



Figure 1.17. DFT simulation results of LIG-based catalyst.

Atomic structures and nonequivalent sites at graphene edges with (a) oxygen adsorbed hexagon marked as hex-O-A, -B, -C, -D, (b) oxygen adsorbed pentagon as pen-O-A, -B, -C, (c) hexagon as hex-A, -B, (d) pentagon as pen-A, -B. Gray and red balls represent carbon and oxygen atoms, respectively. (e) Gibbs free energy diagrams for OER on nonequivalent graphene edge sites in alkaline solution under conditions of pH 14 and the maximum potential allowed by thermodynamics. Figure credit to Luqing Wang and Prof. Yakobson.







Figure 1.18. OER intermediates adsorption structures on edge sites.

(a) Oxygen adsorbed hexagon marked as hex-O-A, -B, -C, -D, (b) oxygen adsorbed pentagon as pen-O-A, -B, -C and (c) hexagon as hex-A, -B and pentagon as pen-A, -B. Gray and red balls represent the carbon and oxygen atoms, respectively. Figure credit to Luqing Wang and Prof. Yakobson.

sites	$\Delta G_{\max}$ (eV)	sites	$\Delta G_{\max}$ (eV)
hex-A	1.55	pen-A	2.59
hex-B	1.32	pen-B	1.27
hex-O-A	2.66	pen-O-A	1.52

hex-O-B	1.42	pen-O-B	1.42
hex-O-C	0.49	pen-O-C	0.72
hex-O-D	1.78		

Table 1.4. OER catalytic sites at graphene edges and the corresponding  $\Delta G_{\text{max}}$ .

In addition to the thermodynamic analysis, we focused on the reaction kinetics of LIG-O since the reaction is energetically favorable at potentials beyond the onset. The generally considered four-electron oxidation pathway for OER in alkaline is shown in **Equation 1.7** (Experimental Section):<sup>36, 63</sup>

 $M + OH^{-} \rightarrow M - OH^{*} + e^{-} \cdots (a)$  $M - OH^{*} + OH^{-} \rightarrow M - O^{*} + e^{-} \cdots (b)$  $M - O^{*} + OH^{-} \rightarrow M - OOH^{*} + e^{-} \cdots (c)$  $M - OOH^{*} + OH^{-} \rightarrow M + H_{2}O + O_{2} + e^{-} \cdots (d)$ 

#### Equation 1.7. Proposed OER mechanistic pathways.

where M is the active site and the star (\*) means it is a surface state. The Tafel slope analysis (Experimental Section) demonstrates that **Equation 1.7**a is the rate determining step (RDS) for LIG-A whereas **Equation 1.7**b is the RDS for LIG-O. This result is intuitively understandable and further confirmed by the electrochemical chemical impedance<sup>34</sup> (Experimental Section) and the estimation of

the adsorption of OER intermediates (**Figure 1.14**d).<sup>35</sup> As shown in **Figure 1.19**, the charge transfer resistance ( $R_{CT}$ ) of LIG-O greatly decreased from more than 10000  $\Omega$  to ~10  $\Omega$  as the potential exceeded the onset potential, suggesting the efficient charge transfer between the electrode and the electrolyte. Conversely, the  $R_{CT}$  of LIG-A remained as high as 1000  $\Omega$  even at a higher potential of 1.65 V. The OER intermediate surface coverage ( $\theta$ ) was calculated from the capacitance of the intermediate adsorption ( $C_{ads}$ ).<sup>35</sup> Since the  $C_{ads}$  was normalized by EASA, the result shows the intrinsic ability of LIG-O and LIG-A for adsorbing the intermediates. **Figure 1.20** shows the  $C_{ads}$  at different potentials where LIG-O had much higher  $C_{ads}$  than LIG-A, especially at the potentials beyond the OER onset. We further calculated the  $\theta$  by integrating the  $C_{ads}$  with potential as in **Equation 1.6** (Experimental Section):<sup>19, 35</sup>

$$C_{\rm ads}(E) = \sigma \; \frac{{\rm d}\theta(E)}{{\rm d}E}$$

#### **Equation 1.6. Determination of the** *Cads*.

where  $\sigma$  is the charge density for a monolayer coverage and is assumed to be constant and the same for LIG-O and LIG-A. LIG-O has much higher  $\theta$  value than LIG-A, which is consistent with the OER activity. As for LIG-A, the low C=O content not only limited the number of active sites, but also hindered the first OER step (**Equation 1.7**a) resulting in a high Tafel slope of 117 mV dec<sup>-1</sup>, while LIG-O benefited from the high C=O content, and the Tafel slope is as low as 49 mV dec<sup>-1</sup> (**Figure 1.21**). Furthermore, we estimated the apparent activation energy (*E*<sub>app</sub>) of the RDS assuming that the velocity of OER was solely dominated by the RDS.<sup>64, 65</sup> The data are summarized in **Figure 1.14** and **Figure 1.22** where  $E_{app}$  was extracted from the Arrhenius plots. Increasing the temperature slightly increased the current density of both LIG-O and LIG-A. However, the  $E_{app}$  of LIG-A was ~15 kJ mol<sup>-1</sup> higher than that of LIG-O. The effect of overpotential on the  $E_{app}$  was further deduced (assuming the symmetry factor  $\beta = 0.5$  and the RDS is not thermodynamically limited) to yield the intrinsic activation energy ( $E_{int}$ ) as shown in **Figure 1.22**.<sup>38</sup> The  $E_{int}$  of LIG-O is significantly lower than that of LIG-A by ~20 kJ mol<sup>-1</sup>, indicating that the velocity of the RDS of LIG-O is ~3000 times higher than that of LIG-A under the same overpotential at room temperature. As has been discussed, the carbon atoms near C=O are the predominate active sites for OER, thus the concentration of C=O also has significant effect on the OER reaction kinetics not only by inducing the active sites, but also by facilitating the adsorption of OER intermediates and lowering the activation energy.



Figure 1.19. EIS analysis of LIG-O and LIG-A.

Nyquist plots of (a) LIG-O and (b) LIG-A. The fitted  $R_{CT}$  and  $R_s$  of (c) LIG-O and (d) LIG-A at different potentials.



Figure 1.20. *C*<sub>ads</sub> (normalized by EASA, μF cm<sup>-2</sup>) of LIG-O and LIG-A.



Figure 1.21. Tafel slope of LIG-O at different overpotentials.



Figure 1.22. OER reaction kinetics of LIG-O and LIG-A.

# (a) LSV curves of LIG-A recorded at different temperature and (b) Arrhenius plots fitted at different overpotentials; the activation energy fitting results for (c) LIG-A and (d) LIG-O.

The oxidation of LIG promoted the OER activity and improved the ORR activity. The ORR performance was characterized by CV in O<sub>2</sub>-saturated 0.1 M KOH (**Figure 1.23**). Both the LIG-O and LIG-A showed a reduction peak. The onset potential of LIG-A was 0.68 V with a peak potential at 0.46 V, while the onset and peak potentials of LIG-O were 0.77 and 0.60 V, respectively. The positively shifted

potentials indicate the improved ORR performance of LIG-O, which was also evidenced by the increased area of the CV curve. The ORR kinetics was investigated using the Koutecký-Levich equation and rotating ring-disk electrodes (RRDE), respectively (**Figure 1.23, Figure 1.24** and **Figure 1.25**).<sup>66</sup> The Tafel slope of LIG-O is as low as 90 mV dec<sup>-1</sup>. The electron transfer number *n* of LIG-O was calculated to be 4.0 at 0.6 V, suggesting an efficient four-electron transfer pathway to generate OH<sup>-</sup>. However, *n* decreased to 2.8 as the potential decreased to 0.4 V, indicating the coexistence of a pathway producing H<sub>2</sub>O<sub>2</sub>. In comparison, LIG-A has a *n* of 2.5-2.8 through 0.6 to 0.4 V. The decrease in *n* was caused by the two-electron transfer process on the pristine carbon surfaces.<sup>67, 68</sup> This observation suggested that both LIG-O and LIG-A underwent the four-electron transfer pathway while LIG-O showed an enhanced activity. Additionally, the LIG-O has shown good structural stability through the OER and ORR tests.



Figure 1.23. The ORR performance of LIG-O.

(a) CV curves of LIG-O and LIG-A recorded in 0.1 M KOH with Ar or  $O_2$  bubbling at 50 mV s<sup>-1</sup>. (b) LSV curves of LIG-O at different rotating speed in 0.1 M KOH with  $O_2$  bubbling.



Figure 1.24. Reaction kinetics of the ORR of LIG-O.

(a) Koutecký-Levich plots and (b) Tafel plots of LIG-O for ORR. (c) Long-term stability of LIG-O for ORR, inset shows the LSV curve at 900 rpm. (d) The RRDE LSV of ORR and (e) the corresponding  $HO_2^-$  yield and *n*.



Figure 1.25. ORR performance of LIG and LIG-A.

LSV curves for ORR at different rotation speed and the Koutecký-Levich plots of (a, b) LIG and (c, d) LIG-A, respectively.



Figure 1.26. SEM and Raman characterization of LIG-O after OER and ORR test.

The morphology and graphenic structure were characterized by SEM and Raman, respectively, to reveal the structure of catalysts after OER and ORR test (**Figure 1.26**). The catalysts were scraped off the GC electrode after electrochemical tests for SEM and Raman characterization. The post-OER and post-ORR LIG-O maintained the porous structure as the pristine LIG-O. Similarly, Raman spectra shows the characteristic multilayer graphene structure for pristine, post-OER and post-ORR LIG-O. The results showed nearly no significantly change in the structure of the LIG-O, regarding the surface morphology and graphenic structure.

The electrochemical performance of LIG-O in OER and ORR highlighted its potential use in Li-O<sub>2</sub> batteries since a bifunctional material is the prerequisite, especially for the oxygen evolution from the decomposition of Li<sub>2</sub>O<sub>2</sub>.<sup>69</sup> The electrocatalytic activity of LIG-0 was examined in a Li-O<sub>2</sub> battery. The device structure is shown in **Figure 1.27**a. The CV curves of the battery, which was tested in Ar and O<sub>2</sub> atmosphere at a scan rate of 0.5 mV s<sup>-1</sup>, are shown in **Figure 1.28**. The battery showed significantly increased current with redox peaks in O<sub>2</sub> when compared to the results in Ar. The potentials of  $Li_2O_2$  formation and decomposition were 2.76 and 3.49 V, respectively, which are very close to the theoretical potential of 2.96 V, indicating the high activity of the LIG-O cathode. The battery was further characterized by galvanostatic discharge/charge tests as shown in **Figure 1.27**b. Despite the similar overpotential in the discharge process, LIG-O showed a remarkably lowered overpotential of 0.63 V, which was much lower than the overpotential of 1.01 V from the pristine LIG. Additionally, LIG-O showed cycle stability superior to that of LIG and commercial Pt/C as depicted in **Figure 1.29**. LIG showed increased overpotential in both the charge and discharge processes as the cycle number increased. The LIG-O had much smaller changes in overpotential through 20 cycles. The decomposition of Li<sub>2</sub>O<sub>2</sub> at lower potential is of great importance for improving the roundtrip efficiency of batteries. A demonstration of the LIG-O Li-O<sub>2</sub> battery is presented in **Figure 1.29**d, where a LED (NTE30105, 2.8 V, 25 mA) was lit by one cell. Due to the high activity of LIG-O, it is probable that the
performance of LIG-O could be further improved by optimization for practical utilization.



Figure 1.27. Li-O<sub>2</sub> battery using LIG-O as the cathode catalyst.

a) Schematic drawing of the structure of  $Li-O_2$  battery with LIG-O as the cathode and b) the charge/discharge profle of the 5th cycle of a battery at 0.16 A g<sup>-1</sup>.





Figure 1.28. CV curves of the Li-O<sub>2</sub> battery with LIG-O cathode at 0.5 mV s<sup>-1</sup>.

Figure 1.29. Cycling performance of the Li-O<sub>2</sub> batteries.

(a) LIG-O, (b) LIG and (c) Pt/C cathode at a current density of 0.16 A  $g^{-1}$ . (d) Illustration of the Li-O<sub>2</sub> battery with LIG-O cathode for lighting a yellow-green LED.

#### 1.2.3. Conclusion

In summary, we prepared oxidized LIG-O as an efficient catalyst for oxygen electrocatalysis. The oxidation of LIG with intrinsic high surface area produces abundant active sites for electrocatalysis, leading to the excellent OER/ORR activity. Additionally, the LIG-O is particularly advantageous for the  $Li_2O_2$  decomposition that can dramatically lower the overpotential of the charging process by ~380 mV. The outstanding OER performance of LIG-O is rationalized by the oxygen-containing groups (e.g. C=O) that enhance the adsorption of OER intermediates and facilitate the rate-determining step. Benefiting from its high performance with low cost and facile preparation, LIG-O is a promising alternative to metal-based catalysts for water splitting, metal-air/O<sub>2</sub> batteries and many other applications. Our findings lead to a better understanding of the catalytic mechanism of LIG derived materials as well as further improvements in the catalytic activity of surface-oxidized carbon nanomaterials.

#### **1.3. Experimental Contributions**

**Muqing Ren** designed the experiments, prepared the samples, conducted part of the characterizations including SEM, TEM, BET and battery test. Jibo Zhang designed parts of the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, ICP-OES, electrochemical measurements and etc. Luqing Wang conducted the theoretical calculation and analysis. Yilun Li helped in SEM and TEM.

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### Chapter 2

## In Situ Synthesis of Efficient Water Oxidation Catalysts in Laser-Induced Graphene

This chapter was entirely copied from reference 70.

#### **2.1. Introduction**

Electrically splitting water into H<sub>2</sub> and O<sub>2</sub> offers an attractive method for renewable energy storage.<sup>71-73</sup> However, the oxidation half reaction of water splitting, which is known as the oxygen evolution reaction (OER),<sup>74-76</sup> is kinetically unfavorable and suffers from high overpotential and energy loss as compared with the reduction half reaction, the hydrogen evolution reaction (HER).<sup>77-79</sup> Noble metal oxides such as IrO<sub>2</sub> and RuO<sub>2</sub> have shown outstanding catalytic performance in OER, but the large-scale application is restricted by their high cost and low abundance.<sup>14</sup>, <sup>80</sup> Alternatively, first-row transition metal oxides and hydroxides have garnered attention for their low cost, high activity and stability in basic solutions. Co-/Ni-/Febased OER catalysts have undergone extensive research in the past decade.<sup>44, 81, 82</sup> Among the various materials, NiFe-based catalysts (oxides and oxyhydroxides) stand out due to their superior performance, showing low onset potentials, low Tafel slopes and excellent durability.<sup>83-86</sup> Generally, the NiFe catalysts were synthesized by solution-based methods such as co-precipitation,<sup>87, 88</sup> solvothermal and hydrothermal reaction<sup>89, 90</sup> and electrodeposition.<sup>91, 92</sup> In a recent work, Müller *et al.* demonstrated an alternative approach using pulsed-laser ablation in liquids to synthesize NiFe layered double hydroxides (LDH) that showed an impressively low overpotential of 260 mV at 10 mA cm<sup>-2</sup> for OER.<sup>93, 94</sup> However, there are very few reports on the direct solid phase synthesis of efficient OER catalysts. A facile and scalable synthetic route to NiFe catalysts is still in demand.

Recently, our group developed a straightforward method to grow porous graphene by direct laser writing on a polyimide (PI) sheet to produce laser-induced graphene (LIG).<sup>28, 29</sup> We further improved the method to prepare metal oxide nanoparticle/graphene composites from metal-complex containing PI films for the oxygen reduction reaction.<sup>95</sup> But the tedious procedures to incorporate the metal species in poly(amic acid), the PI precursor, followed by thermal curing and postannealing, diminished the accessibility for practical applications. We present here a significantly improved strategy for synthesizing metal oxide/graphene hybrid materials as highly efficient catalysts for OER. By pre-forming LIG, then merely

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adding the proper metal precursors to the existing LIG layer, followed by re-lasing, the nucleation of metal oxide nanoparticles ensured that were uniformly embedded in the LIG. Benefiting from this solid phase synthetic method, we prepared a series of NiFe oxide/graphene hybrid catalysts (NiFe/LIG) that showed remarkably high OER activity, among which the best catalyst had a remarkably low overpotential of 240 mV at 10 mA cm<sup>-2</sup> with a Tafel slope of 32.8 mV dec<sup>-1</sup> and excellent stability. Moreover, the method is also applicable for non-LIG/PI substrates such as carbon fiber paper (CFP) to a directly fabricated self-supported catalytic electrode.

In addition to the high OER activity of the NiFe/LIG catalysts, the simplified method presented meets the requirement of roll-to-roll production and could be applied to many metal precursors regardless of their solubility and compatibility with the precursor of PI.<sup>95</sup> The composition of nanoparticles is conveniently tunable by altering the precursor for applications in various electrocatalytic reactions such as hydrogen evolution and oxygen reduction.

## 2.2. In Situ Synthesis of Efficient Water Oxidation Catalysts in Laser-Induced Graphene

#### 2.2.1. Experimental Section

#### 2.2.1.1. Material Synthesis

**Preparation of LIG.** Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser cutter

system (10.6  $\mu$ m, Universal XLS10MWH laser cutter platform) on the Kapton<sup>®</sup> PI in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2×2 cm<sup>2</sup> square.

**Preparation of the catalysts.** 1 M NiSO<sub>4</sub> and 1 M FeCl<sub>3</sub> solutions were prepared with deionized water. Then the mixture solutions with different molar ratios ([Ni<sup>2+</sup>]: [Fe<sup>3+</sup>]) were prepared, and the total concentration of metal cations ([Ni<sup>2+</sup>] + [Fe<sup>3+</sup>]) was kept at 1 M. The as-prepared LIG ( $2 \times 2 \text{ cm}^2$ ) was treated in the UV-ozone cleaner (Boekel Model 135500) for 3 min to ensure the wettability of LIG with aqueous solutions. 80 µL of the solutions were dropped uniformly onto the LIG. The soaked LIG (on PI) was dried in air at room temperature overnight and then vacuum (~120 mm Hg) dried for 3 h. The LIG was lased again on the same LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). Then the powder was scratched off from the PI using a spatula and collected for characterization.

**Preparation of the NiFe/CFP.** A piece of carbon fiber paper (CFP, ~1 × 1 cm<sup>2</sup>, FuelCellStore) was treated by a UV-ozone cleaner (Boekel Model 135500) for 5 min to improve the wettability. Then 80 µL of the precursor solution ([Ni<sup>2+</sup>]: [Fe<sup>3+</sup>], 1:1) was dropped onto the CFP. The CFP was dried in air at room temperature overnight and then transferred into a vacuum chamber (~120 mm Hg) and dried at room temperature for 6 h. The CFP was scribed by the laser beam with 3% of full power, 5% of full speed and an image density of 6. The area of the lased pattern was  $7 \times 7 \text{ mm}^2$ .

#### 2.2.1.2. Material Characterization

**General characterization.** SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images and elemental mapping images were obtained by a JEOL 2100F field emission gun transmission electron microscope. XPS analysis was done on a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. The XPS spectra were taken from the as-prepared catalysts on PI. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was carried out using a Perkin Elmer Optima 8300 instrument.

**Electrochemical measurements.** For the preparation of the working electrode, 4 mg of the carbon-metal catalyst composite and 80 µL of 5 wt% Nafion solution were mixed with 1 mL water/ethanol (4/1, v/v) followed by 2 h bath-sonication (Cole Parmer, model 08849-00) to form a homogeneous ink. 5 µL of the ink was dropped onto a glassy carbon electrode (3 mm in diameter) and dried in air at room temperature (the catalyst loading is ~0.265 mg cm<sup>-2</sup>). The electrochemical measurements were carried out in a 3-electrode configuration using CHI 608D electrochemical workstation. Pt plate and Hg/HgO (in 1 M KOH) were used as the counter and reference electrode, respectively. The tests regarding oxygen evolution were done in 1 M KOH with 95% iR compensation. The potential was normalized with RHE.

The EASA is calculated from the double-layer capacitance of the catalyst. Typically, the CV curves of LIG catalysts were recorded in the non-Faradic region (-0.05 to 0.05 V *vs* Hg/HgO in 1 M KOH) at scan rates ranging from 10 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup>. The geometric current density  $j_{GSA}$  solely originates from the charging/discharging of the double layer capacitance as given by the following **Equation 2.1** and **Equation 2.2**:

$$j = C_{\rm dl} \cdot \frac{dV}{dt}$$

#### Equation 2.1. Calculation of the C<sub>dl</sub> of NiFe/LIG catalysts.

EASA is calculated based on:

$$EASA = \frac{C_{dl}}{C_s}$$

#### Equation 2.2. Calculation of the EASA of NiFe/LIG catalysts.

where  $C_s$  is the ideal specific capacitance of a smooth planar surface. The geometric surface area (GSA) of the glassy carbon electrode is 0.07 cm<sup>2</sup>. The value of  $C_s$  is considered as 40 µF cm<sup>-2</sup>, and the *j* is averaged by the charge and discharge current recorded at 0 V (*vs* Hg/HgO).

**Fe-incorporation test of Ni/LIG.** This test was done on Ni/LIG. The catalyst (on glassy carbon electrode) was cycled from 1.21 to 1.53 V (*vs* RHE) in 1 M KOH

with slow magnetic stirring (60 rpm). The Fe-containing electrolyte was prepared by adding 100  $\mu$ L of 1 M FeCl<sub>3</sub> into 100 mL 1 M KOH and then the suspension was stirred for 6 h. The excess Fe precipitated, ensuring soluble Fe<sup>3+</sup> saturated the 1 M KOH solution. For the Fe-incorporation test, the electrode was cycled in 1 M KOH for 20 cycles prior to further cycling in the Fe-containing electrolyte.

#### **Calculation of the turnover frequency (TOF).** The turnover frequency

represents the number of catalytic cycles occurring at the active center per unit time and is generally calculated as: TOF (s<sup>-1</sup>) = (number of oxygen turnover)/(number of active sites) = (j/4F)/n, where *j* is the current density at a specific overpotential (e.g. 300 mV) and *n* is the number of active sites calculated based on the ICP-OES result. The number of oxygen turnover is calculated with **Equation 2.3**:

$$(j\frac{\mathrm{mA}}{\mathrm{cm}^2})(\frac{1\frac{\mathrm{C}}{\mathrm{s}}}{1000 \mathrm{mA}})(\frac{1 \mathrm{mol} e^-}{96485 \mathrm{C}})(\frac{1 \mathrm{mol} O_2}{4 \mathrm{mol} e^-}) \times N_A$$

Equation 2.3. TOF calculation of the NiFe/LIG catalysts.

#### 2.2.2. Result and Discussion

The *in situ* synthesis of NiFe/LIG catalysts were done by a laser assisted method as shown in **Figure 2.1**Error! Reference source not found. Briefly, the LIG was patterned on a piece of PI sheet followed by UV-ozone treatment to increase the

hydrophilicity. Then the precursor solution containing Ni<sup>2+</sup> and Fe<sup>3+</sup> was dropped onto the LIG. Due to the increased hydrophilicity and porosity of LIG, the solution was uniformly adsorbed by the carbon structure. After drying, we lased the PI sheet again atop the original LIG. The extremely high local temperature (>2500 °C) generated while the underlying PI film was being graphitized facilitates the nucleation process of the metal ions, leading to a metal oxide/graphene composite structure. The NiFe/LIG catalysts were prepared based on 3 different Ni:Fe molar ratios of the precursor solutions,<sup>83</sup> 2:1 for NiFe/LIG-1, 1:1 for NiFe/LIG-2 and 1:2 for NiFe/LIG-3, along with Ni/LIG (1:0) and Fe/LIG (0:1) for comparison. Unlike the previously reported method, the current method does not require the solubility/compatibility of metal precursors in poly(amic acid) solutions, nor the utilization of chemical vapor deposition system (CVD).<sup>95</sup> All of the procedures can be directly done on the PI sheet in the ambient environment and water solvent.



Figure 2.1. Preparation of the NiFe/LIG catalysts and the SEM images.

(b) NiFe/LIG-1, (c) NiFe/LIG-2 and (d) NiFe/LIG-3. The scale bar represents 10  $\mu m.$ 



Figure 2.2. SEM images of NiFe/LIG-1.



Figure 2.3. SEM images of NiFe/LIG-2.



Figure 2.4. SEM images of NiFe/LIG-3.

The scanning electron microscopy (SEM) images shown in **Figure 2.1**, **Figure 2.2**, **Figure 2.3 and Figure 2.4**, illustrate the morphology of the catalysts. Regardless of the different Ni:Fe ratio, the catalysts show a highly porous structure with no nanoparticle aggregates. The catalysts are powders for which the sheet conductivity could not be measured, but prior work shows the porous LIG graphitic structure maximizes the exposure of the surface active sites and contributes to a good electric conductivity for electrochemical reactions.



Figure 2.5. TEM images and Raman spectra of the NiFe/LIG catalysts.

(a) NiFe/LIG-1, (b) NiFe/LIG-2 and (c) NiFe/LIG-3. The scale bar represents 10 nm.

The transmission electron microscopy (TEM) image shown in **Figure 2.5** revealed the nanoparticle/graphene hybrid structure. The nanoparticles are well embedded in the graphene structure and surrounded by a few layers of graphene. For NiFe/LIG-1 and NiFe/LIG-3, the size of the nanoparticles is ~10-15 nm. NiFe/LIG-2 has a smaller nanoparticle size of ~5-12 nm, indicating a higher surface area compared to NiFe/LIG-1 and NiFe/LIG-3. The NiO phase planar spacing of the (211) plane (0.21 nm) was clearly observed from the high-resolution images. **Figure 2.5**d demonstrates the graphene structure in the catalysts (see also **Figure 2.6**).<sup>96,97</sup> The clearly identified D, G and 2D peaks suggest the existence of defected or bent multi-layer graphene as the characteristic sign of LIG,<sup>98</sup> which is consistent with the TEM observations. The results confirmed that the nanoparticles and LIG were formed during the laser scribing.



Figure 2.6. Powder XRD diffraction pattern of the catalysts and supplementary Raman spectra and TEM images.

Solid rhombus ( $\blacklozenge$ ) represents the pattern from NiO, open rhombus ( $\diamondsuit$ ) represents the pattern from NiO, and solid roundness ( $\blacklozenge$ ) represents the pattern from Fe<sub>2</sub>O<sub>3</sub>. (b) Raman spectra of Ni/LIG and Fe/LIG. And the TEM images of (c) Ni/LIG and (d) Fe/LIG.



Figure 2.7. XPS analysis of the NiFe/LIG catalysts.

# The high-resolution spectra in (a) Ni 2p, (b) Fe 2p, (c) C 1s and (d) O 1s regions (The satellite peak is abbreviated as sat.).

X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze the elemental composition and chemical valence states of the catalysts. The results are summarized in **Figure 2.7**. The Ni  $2p_{3/2}$  region of the NiFe/LIG catalysts shows two main peaks at ~852.8 and ~855.8 eV that can be attributed to the Ni<sup>0</sup> and Ni<sup>2+</sup> with the split spin-orbit components at ~870.1 and 873.1 eV, respectively.<sup>99</sup> The Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  peaks locates at 710.8 and 729.3 eV alone with the satellite peaks, which are the characteristic binding energies of Fe<sup>3+</sup>.<sup>100</sup> These features indicate the existence of small amount of elemental Ni in the catalysts that might be caused by the reduction at high temperature induced by the laser. However, the Ni<sup>0</sup> would be oxidized to Ni<sup>2+</sup> and further to Ni<sup>3+</sup> under anodic conditions prior to the OER potentials.<sup>82</sup> The C 1s spectra show a characteristic peak of LIG at 284.5 eV, corresponding to the sp<sup>2</sup> carbon from graphene. The O 1s spectra has two distinct peaks: the peak at ~532 eV originates from the oxygen-containing moieties such as C-O and C=O from LIG; and the peak at ~530 eV corresponds to the metal oxides. In addition to the XPS measurement, the ratios of Ni:Fe are determined by the inductively coupled plasma optical emission spectrometry (ICP-OES). The molar ratios of Ni:Fe are 61:39, 46:54 and 33:67 for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively.

Although the signal to noise ratio of the XRD patterns in **Figure 2.6** is low, we can still find the characteristic peaks that help to understand the bulk composition of the catalysts. The broad peak at ~26° corresponds to the (002) planes of multilayer graphene (LIG). Fe/LIG shows a broad (311) peak at ~35°, however, this peak becomes very weak and nearly indistinguishable from the noise in the NiFe/LIG catalysts. This result shows that most of the Fe species are not in the form of monometallic oxide (Fe<sub>2</sub>O<sub>3</sub>). Ni/LIG shows characteristic peaks from both Ni0 ((110) peak at ~39° and (111) peak at ~44°) and NiO ((111) at ~37° and (200) at 43°), both approximately the same height. This is consistent with the XPS result (**Figure 2.7**) and TEM images (**Figure 2.6**). Comparison of the Ni<sup>0</sup> peak in the Ni/LIG catalyst to the same position in the NiFe/LIG catalysts shows a reduction in size in the NiFe/LIG catalyst, especially when compared to the NiO peak from the NiFe/LIG catalysts. **Figure 2.6** shows the Raman spectra of the Fe/LIG and Ni/LIG catalysts for comparison to the Raman spectra for the NiFe/LIG catalysts in **Figure** 

**2.5**. The clearly identified D, G and 2D peaks suggest the characteristic multi-layer graphene structure of LIG which is consistent with the TEM images.



Figure 2.8. TEM elemental mapping of the catalysts.

The elemental maps of Ni and Fe (**Figure 2.8**) show that the distribution of Fe species overlaps well with that of the Ni, suggesting that the nanoparticles consist of both Ni and Fe. The XRD result (**Figure 2.6**a) indicates that there are few separate phases of Fe in the NiFe/LIG catalysts, in contrast to those found in the Fe/LIG (Fe<sub>2</sub>O<sub>3</sub>). Also, the high resolution TEM images of the NiFe/LIG catalysts indicate little Fe<sub>2</sub>O<sub>3</sub>, but the characteristic lattice plane spacing of NiO was observed.

By combining the results from high resolution TEM, XRD and elemental mapping, we conclude that the Fe species are mainly doped in the NiO nanoparticles.



Figure 2.9. OER performance characterized in 1 M KOH.

(a) LSV curves recorded at 2 mV s<sup>-1</sup>. (b) Tafel plots calculated from the LSV curves. (c) Comparison of the Tafel slopes and  $\eta_{10}$  of the catalysts with IrO<sub>2</sub> nanoparticles<sup>101</sup> ( $\diamondsuit$ ) and 3D Ir<sup>102</sup> ( $\ddagger$ ). (d) Stability test, potential profile of the catalysts for bulk OER at 10 mA cm<sup>-2</sup>.

The OER activity of the NiFe/LIG catalysts along with Ni/LIG and Fe/LIG was assessed in 1 M KOH using a 3-electrode configuration. **Figure 2.9**a shows the linear sweep voltammetry (LSV) curves recorded at 2 mV s<sup>-1</sup>. The NiFe/LIG catalysts

exhibited much higher activities than either Ni/LIG or Fe/LIG. The OER onset potentials of the NiFe/LIG catalysts are  $\sim$ 210 mV despite overlapping with the Ni oxidation peak.<sup>103</sup> In contrast, the onset potentials of Ni/LIG and Fe/LIG are much higher at 250 and 290 mV, respectively. The current density (*j*) of NiFe/LIG-2 reached 10 mA cm<sup>-2</sup> at a remarkably low overpotential ( $\eta_{10}$ ) of 240 mV. The  $\eta_{10}$  of NiFe/LIG-1 and NiFe/LIG-3 are 266 and 279 mV, respectively. Conversely, the  $\eta_{10}$  of Ni/LIG is very high at 380 mV and that of Fe/LIG is even higher at 395 mV. The NiFe/LIG-1 and NiFe/LIG-2 rose to *j* of 100 mA cm<sup>-2</sup> at very low overpotentials of 324 and 309 mV (Figure 2.10), indicating the intrinsic high activity of the catalysts. Figure 2.11 shows the galvanostatic OER performance of NiFe/LIG-2. The catalyst exhibited excellent stability at *j* ranging from 10 to 100 mA cm<sup>-2</sup>. It should be noted that a slight variation of the potential during the bulk OER is reasonable due to the formation and desorption of bubbles on the electrode surface. The reaction kinetics was characterized by the Tafel plots shown in Figure 2.9b.63 The binary metal oxide based catalysts have shown significantly improved OER kinetics over the monometallic oxides. The NiFe/LIG-2 has an impressively low Tafel slope of 32.8 mV dec<sup>-1</sup>, followed by 33.4 mV dec<sup>-1</sup> for NiFe/LIG-1 and 36.6 mV dec<sup>-1</sup> for NiFe/LIG-3.

**Figure 2.9**c provides a straightforward comparison of the catalysts with the benchmarking Ir-based catalysts in terms of  $\eta_{10}$  and Tafel slope. The NiFe/LIG catalysts demonstrated much higher activity than the IrO<sub>2</sub> nanoparticles.<sup>101</sup> The NiFe/LIG-2 even have a comparable performance to that of the 3D Ir catalyst.<sup>102</sup> A

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detailed comparison of NiFe/LIG catalysts with state-of-the-art Ni-Fe OER catalysts is summarized in **Table 2.1**, where the NiFe/LIG catalysts stand out for their superior OER activity in addition to the simple and feasible preparation method. In addition to for the high OER activity, the NiFe/LIG catalysts showed excellent durability throughout the test (**Figure 2.9**d). After 15000 s of bulk OER at 10 mA cm<sup>-2</sup>, the  $\eta_{10}$  slightly increased by 11, 12 and 34 mV for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively.

Catalyst	Preparation method <sup>a</sup>	Tafel Slope (mV dec <sup>-1</sup> )	$\eta_{10 \text{ mA cm}^{-2}}$ (mV)	
NiFe/LIG-1	LIG	33.4	266	
NiFe/LIG-2	LIG	32.8	240	
NiFe/LIG-3	e/LIG-3 LIG 36.6		279	
NiFe LDH <sup>93</sup>	PLAL	47.6	280	
Ni-Fe/3D-ErGO <sup>104</sup>	ED	33	259	
Ni-Fe <sup>104</sup>	ED	58	331	
NiFe LDH <sup>101</sup>	PC	67	347	
NiFe LDH/CNT hybrid <sup>89</sup>	PC	31	247	
Fe:Ni(OH) <sub>2</sub> film <sup>105</sup>	IA	40	280	

FeNi LDH <sup>90</sup>	РС	48	232
NiFe LDH exfoliated <sup>101</sup>	EX from PC	40	302

Table 2.1. Comparison of the NiFe/LIG catalysts with recently reported OER catalysts.

<sup>a</sup>Abbreviations for the methods: LIG, this work; PLAL, pulsed laser ablation in liquid; ED, electrodeposition; PC, precipitation; IA, iron incorporation by aging; EX, exfoliation.



Figure 2.10. LSV curves of the catalysts at high potential.



Figure 2.11. Galvanostatic OER performance of NiFe/LIG-2 ramping from 10 to 20, 40, 60, 80 and 100 mA cm<sup>-2</sup> in 1 M KOH.



Figure 2.12. Electrochemical analysis of the catalysts.

(a) CV curves recorded in 1 M KOH at 2 mV s<sup>-1</sup>. (b) Geometric current density ( $j_{GSA}$ ) at 0 V (vs Hg/HgO) plotted against the scan rate for the determination of  $C_{dl.}$  (c) EIS of the catalysts. Inset shows the equivalent circuit to simulate the  $R_s$  and  $R_{CT.}^{106}$  (d) TOF and mass activity of the catalysts at 300 mV overpotential.

The results above have shown that the NiFe/LIG catalysts have much lower thermodynamic and kinetic barriers than either Ni/LIG or Fe/LIG. In order to further understand the high activity of the catalysts, we performed cyclic voltammetry measurements (CV) as depicted in **Figure 2.12**a. The data were collected at a low scan rate (2 mV s<sup>-1</sup>) to ensure a quasi-equilibrium measurement. There is no feature associated with the change in the oxidation state of Fe as suggested by previous reports.<sup>83</sup> On the contrary, a pair of anodic and cathodic waves was observed in the Ni-containing catalysts, which was attributed to the redox of Ni<sup>2+</sup> to higher oxidation states (Ni<sup>3+</sup> and Ni<sup>4+</sup>).<sup>107</sup> The redox waves shifted anodically and decreased gradually as the Fe content increased. For NiFe/LIG-2 and NiFe/LIG-3 (where the Fe content is 54% and 67%, respectively), the anodic wave started to overlap with the OER current. It is evident that the presence of Fe suppressed the oxidation of Ni<sup>2+</sup> to higher oxidation states, however, the underlying mechanism is still under debate.<sup>107</sup> Several hypotheses have been proposed, for example, the decreased affinity to oxygen of the Ni surface<sup>108</sup> and the destabilization of Ni<sup>3+</sup> species in presence of Fe<sup>3+,109</sup> Additionally, it was also revealed that the effective conductivity of the catalysts was sensitive to the Fe content, which might also contribute to the redox behavior of the NiFe-based catalyst.<sup>107</sup>

Our results are in accord with the NiFe catalysts synthesized by solutionbased methods where the maximum performance is achieved with Fe content of ~15-50% while further increasing Fe content would decrease the activity.<sup>110</sup> In light of recent studies regarding the crucial effect of Fe on the local activity of Ni(OH)<sub>2</sub>/NiOOH,<sup>111</sup> we carried out a Fe-incorporation test of Ni/LIG (**Figure 2.13**). In the electrolyte without intentionally added Fe<sup>3+</sup>, the Ni/LIG showed nearly no increase in the OER activity (300 mV overpotential) after 300 CV cycles. On the

contrary, an immediate increase in the OER activity was observed when the electrode was moved into the Fe-containing electrolyte, suggesting a rapid Fe incorporation.<sup>111</sup> We also noticed that the change in the OER activity upon gradual Fe incorporation was not directly related to the shifts of the peak position of  $Ni^{2+}/Ni^{3}$  redox. Our findings coincide with the mechanism proposed by Boettcher *et al.*,<sup>111</sup> indicating that the OER activity depends more on the Fe incorporated at the edges/surface defects of Ni(OH)<sub>2</sub>/NiOOH than on the Fe inside the bulk nanoparticles. And it might be the case that the rapid laser heating would lead to more surface defects of the nanoparticles as compared with other solution based methods.<sup>95</sup> It is likely that the Fe sites incorporated at the surface of  $\gamma$ -NiOOH account for the highest activity for their lowest overpotential proposed by theoretical calculations.<sup>108</sup> On the other hand, the measured redox curve of Ni<sup>2+</sup>/Ni<sup>3+</sup> (Figure 2.12a) represents a cumulative result over the bulk nanoparticles and so that the electrochemical behavior of the active sites might be averaged in the CV measurements.



Figure 2.13. Fe-incorporation test of Ni/LIG.

(a) CV curves of Ni/LIG in 1 M KOH without intentionally added Fe. (b) The CV curves of 1<sup>st</sup>, 25<sup>th</sup> and 300<sup>th</sup> cycle from (a). (c) CV curves of Ni/LOH in Fecontaining electrolyte. The initial 20 cycles were recorded in 1 M KOH without intentionally added Fe. (d) The CV curves of 75<sup>th</sup> and 200<sup>th</sup> cycle from (c), and that of NiFe/LIG-2. (e) and (f) show the current density at 300 mV overpotential ( $j_{\eta300}$ ) and anodic Ni<sup>2+</sup>/Ni<sup>3+</sup> peak position ( $E_{anodic}$ ) as a function of the cycle number adapted from (a) and (c), respectively. Recent studies have shown that Fe impurities would readily incorporate into Ni(OH)<sub>2</sub>/NiOOH during electrochemical measurements.<sup>112</sup> **Figure 2.13** and b show the CV curves of Ni/LIG in 1 M KOH with the current density at 300 mV overpotential ( $j_{\eta300}$ ) and anodic Ni<sup>2+</sup>/Ni<sup>3+</sup> peak position ( $E_{anodic}$ ) plotted against the cycles in **Figure 2.13**e. In initial cycles (1~25), the  $E_{anodic}$  shifted to low potential and as peak slightly narrowed and increased. The shift of  $E_{anodic}$  should be due to the formation of more ordered Ni(OH)<sub>2</sub>/NiOOH. After the 25<sup>th</sup> cycle, the  $E_{anodic}$  shifted anodically and the peak decreased gradually. At 300<sup>th</sup> cycle, the  $E_{anodic}$  was 29 mv higher than that of 25<sup>th</sup> cycle. However, the  $j_{\eta300}$  did not show much change during the entire cycling. The mere change in  $E_{anodic}$  could be explained by the presence of trace amount of Fe in the electrolyte and the results are in consistent with a recent study by Boettcher *et al.*<sup>107</sup> Nevertheless, it should be noted that, the trace Fe impurities has little effect on the OER performance of our catalysts since the  $j_{\eta300}$  is far lower than those of the NiFe/LIG catalysts.

The Fe-incorporation test of Ni/LIG was done in the electrolyte with intentionally add Fe<sup>3+</sup> as shown in **Figure 2.13**c. The initial 20 cycles were recorded in 1 M KOH and the subsequent cycles were done in the Fe-containing electrolyte. When the electrode was moved into the Fe-containing electrolyte at 21<sup>th</sup> cycle, immediate increases in both  $E_{\text{anodic}}$  (by 8 mV) and  $j_{\eta300}$  (by 1.5 mA cm<sup>-2</sup>) were observed. Further cycling resulted in the gradual increase of  $j_{\eta300}$  till its maximum value of 12.8 mA cm<sup>-2</sup> at ~75<sup>th</sup> cycle, where the  $E_{\text{anodic}}$  was 22 mV anodically shifted than that of 21<sup>th</sup> cycle. After ~75<sup>th</sup> cycle, the  $E_{\text{anodic}}$  kept increasing while the  $j_{\eta300}$ 

decreased. At 200<sup>th</sup> cycle, the  $E_{\text{anodic}}$  and  $j_{\eta 300}$  were 1.404 V (*vs* RHE) and 7.1 mA cm<sup>-2</sup>, respectively.

In our measurement, the gradually shifted  $E_{\text{anodic}}$  with decreased intensity agreed well with the long-held opinion that Fe suppressed the oxidation of Ni<sup>2+</sup> to higher valence state (+3 and +4).<sup>83</sup> However, the results also revealed that  $j_{\eta 300}$  is not directly related with *E*anodic. As shown in Figure 2.13d, the OER activity of 200<sup>th</sup> cycle was inferior to that of 75<sup>th</sup> cycle, despite the more suppressed Ni<sup>2+</sup>/Ni<sup>3+</sup> redox. In consideration of our catalysts which are nanoparticles with diameter of  $\sim 10-20$ nm embedded in graphene, it is reasonable to assume that the Fe would firstly incorporate at the edges/surface defects, and further move inside of the bulk nanoparticle. On the other hand, the effective conductivity of NiOOH remains high through the potential window and it is not decreased by the Fe incorporation.<sup>107</sup> Therefore, the measured Ni<sup>2+</sup>/Ni<sup>3+</sup> redox would be a cumulative result of the whole nanoparticle. Since the OER activity is more dependent on the surface structure of the heterogeneous catalyst, the immediate change at 21<sup>th</sup> cycle should be induced by the instant Fe incorporation at the edges/surface defects of Ni(OH)<sub>2</sub>/NiOOH. Since the edges/surface defects are gradually incorporated as the cycling continued, the rate of current increase reduced and the  $i_{n300}$  reached the maximum value at~75<sup>th</sup> cycle (**Figure 2.13**f). The decrease of  $j_{\eta_{300}}$  upon further cycling were caused by several reasons, such as the formation of FeOOH phase on the surface of NiOOH and the distorted bulk structure after Fe incorporation. Whereas, since the measured  $E_{\text{anodic}}$  is related to the bulk nanoparticle, it kept increasing as Fe was incorporated.

Our results coincide with the recent study on Ni(OH)<sup>2</sup> thin film,<sup>111</sup> suggesting the effects of Fe on the local structure. The active species based on our catalyst is likely to be the NiOOH with Fe incorporated at the edges/surface defects. And the enhanced activity was attributed to the partial charge transfer between Ni and Fe.<sup>107</sup> It's worth noting that although the efficient catalyst could be prepared by Fe incorporation, our LIG method provides a more convenient and scalable way to produce catalyst with better performance (**Figure 2.13**d).

In addition to the inherent activity of the active sites, the electrochemically active surface area (EASA) is also important to the overall catalytic performance since it determines the total active sites exposed to the electrolyte.<sup>33</sup> Figure 2.12b illustrates the double-layer capacitance (*C*<sub>dl</sub>) calculated from the CV curves (**Figure 2.14**). Benefiting from the porosity and conductivity of LIG, the catalysts have reasonably high C<sub>dl</sub> of 1.76, 3.06 and 1.20 mF cm<sup>-2</sup> for NiFe/LIG-1, NiFe/LIG-2 and NiFe/LIG-3, respectively. And the corresponding EASA are about 44, 76 and 30 cm<sup>2</sup> per  $cm^2$  of the geometric surface area (GSA), respectively. The electrochemical impedance spectrum (EIS) was used to study the reaction kinetics under OER conditions (Figure 2.15).<sup>106</sup> As shown in Figure 2.12c, NiFe/LIG-2 has a remarkably low charge transfer resistance ( $R_{CT}$ ) of 15  $\Omega$  under 280 mV overpotential, and the  $R_{CT}$  further decreased to 8  $\Omega$  under 300 mV overpotential (**Figure 2.15**d). The *R*<sub>CT</sub> of NiFe/LIG-1 and NiFe/LIG-3 are slightly higher as 22 and 66  $\Omega$ , respectively, in concert with their lower activities than that of NiFe/LIG-2. The large EASA is beneficial for the intimate contact of the catalysts with the electrolyte,

along with the exposure of active sites to ensure an efficient charge transfer between the electrode and the electrolyte that contributes to the excellent OER activity.

In order to provide an indication of the activity of a specific site, we calculated the turnover frequency (TOF) by averaging over the total moles of metal ions (Ni and Fe) based on the *j* at 300 mV overpotential.<sup>83</sup> Table 2.2 summarizes data from the NiFe/LIG catalysts and compares it to recently published results. The NiFe/LIG catalysts have comparatively high TOF with a high mass loading of ~0.265 mg cm<sup>-2</sup>. The highest TOF of 0.42 s<sup>-1</sup> is achieved on NiFe/LIG-2 with a *j* of 85.70 mA  $cm^{-2}$  at 1.53 V. The *j* is also of much importance since it demonstrates the specific mass activity of the catalyst, although a higher TOF is usually calculated from low mass loading. Another notable phenomenon is that the carbon-composited catalysts generally have much higher activities than the unsupported ones, and this includes the exfoliated LDHs that have a high surface-volume ratio.<sup>103</sup> As summarized in **Table 2.3**, the catalysts have high current density (86 mA cm<sup>-2</sup>), high TOF (0.42 s<sup>-1</sup>) along with high mass activity (323 mA mg<sup>-1</sup>). The NiFe/LIG catalysts have shown comparable performance to the ones prepared by more elaborate solution-based processes.



Figure 2.14. Determination of the C<sub>dl</sub>.

CV curves recorded at 10, 20, 40, 60, 80 and 100 mV s<sup>-1</sup> of the catalysts.



Figure 2.15. EIS of the catalysts at different overpotentials and the RCT.

Catalysts	<i>j</i> (mA cm <sup>-2</sup> )	TOF (s-1)	Mass loading (mg cm <sup>-2</sup> )
Ni/LIG	0.95	2.0×10 <sup>-3</sup>	~0.265
NiFe/LIG-1	51.99	2.6×10 <sup>-1</sup>	~0.265
NiFe/LIG-2	85.70	4.2×10 <sup>-1</sup>	~0.265
NiFe/LIG-3	28.15	1.1×10 <sup>-1</sup>	~0.265
Fe/LIG	0.20	6.2×10 <sup>-4</sup>	~0.265
NiFe LDH <sup>101</sup>	5.5	1.0×10 <sup>-2</sup>	0.07
NiFe LDH exfoliated <sup>101</sup>	9.35	5.0×10 <sup>-2</sup>	0.07
NiFeO <sub>x</sub> film <sup>112</sup>	1.24	2.1×10 <sup>-1</sup>	0.0012
Fe:Ni(OH) <sub>2</sub> film <sup>105</sup>	25-28	1.5 30 nm of active la	
FeNi LDH <sup>90</sup>	Not reported	2.8×10 <sup>-2</sup>	0.25

FeNi-rGO LDH hybrid <sup>90</sup>	Not reported	9.9×10 <sup>-1</sup>	0.25
NiFe LDH/CNT hybrid	Not reported	5.6×10 <sup>-1</sup>	0.25

Table 2.2. Comparison of catalyst activity with recent published works (1.53 V *vs* RHE).

Catalysts -	Current density (mA cm <sup>-2</sup> )		TOF per active site (s <sup>-1</sup> )		Mass activity (mA mg <sup>-1</sup> )	
	η = 250 (mV)	η = 300 (mV)	η = 250 (mV)	η = 300 (mV)	η = 250 (mV)	η = 300 (mV)
Ni/LIG	0.24	0.95	5.1×10 <sup>-4</sup>	2.0×10 <sup>-3</sup>	0.91	3.57
NiFe/LIG-1	3.40	51.99	1.7×10 <sup>-2</sup>	2.6×10 <sup>-1</sup>	12.81	196.17
NiFe/LIG-2	16.51	85.70	8.0×10 <sup>-2</sup>	4.2×10 <sup>-1</sup>	62.32	323.40
NiFe/LIG-3	1.73	28.15	6.9×10 <sup>-3</sup>	1.1×10 <sup>-1</sup>	6.54	106.20
Fe/LIG	0.06	0.20	1.9×10 <sup>-4</sup>	6.2×10 <sup>-4</sup>	0.22	0.75

# Table 2.3. TOF and mass activity of the catalysts at 250 and 300 mV overpotentials.

The OER performance could be further improved by loading the catalysts on a porous substrate, such as the Ni foam. Benefiting from the high surface area and high conductivity of Ni foam, the NiFe/LIG-2@NF showed a remarkably high *j* of 400 mA cm<sup>-2</sup> at a very low overpotential of 354 mV as shown in **Figure 2.16**a.



Figure 2.16. OER performance of the catalyst loaded on Ni foam and carbon fiber paper.

# (a) LSV curve of the NiFe/LIG-2 loaded on Ni foam (~0.5 mg cm<sup>-2</sup>). (b) The OER performance of NiFe/CFP in 1 M KOH. Inset shows the corresponding Tafel plots.

In addition to the LIG/PI substrate, our method also worked on other compatible substrates. The CO<sub>2</sub> laser is widely used for the manufacturing of carbon fiber based materials due to the significant thermal input from the incident laser beam.<sup>113</sup> Therefore, the thermal effect could be utilized to prompt the nucleation of metal oxides. Following a procedure similar to that for NiFe/LIG, we prepared the free-standing NiFe/CFP electrodes, where the catalyst was formed *in situ* on the CFP through the laser scribing process. **Figure 2.16**b illustrates the excellent OER performance of NiFe/CFP, the onset potential ~1.45 V and *j* reaching 100 mA cm<sup>-2</sup> at 285 mV overpotential with a Tafel slope of 89 mV dec<sup>-1</sup>. These results not only

provide a feasible method for the preparation of self-supported catalytic electrodes, but also demonstrate the wide breadth of the LIG method for the synthesis of various catalysts.

#### 2.3. Experimental Contributions

**Muqing Ren** designed part of the experiments and conducted part of the characterizations including SEM, TEM, XRD and ICP-OES. Jibo Zhang designed part of the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, electrochemical measurements and etc. Yilun Li helped in SEM and TEM.
# Chapter 3

# Laser-Induced Graphene with Bifunctional Catalysts for Metal-Oxygen Batteries

This chapter was entirely copied from reference 114.

# **3.1. Introduction**

The rapid economic development and increasing consumption of carbon fuels have spawned high CO<sub>2</sub> emissions.<sup>115, 116</sup> This increase, coupled with the awareness of climate change, has prompted the development of carbon neutral and renewable energy. Recently, rechargeable metal-O<sub>2</sub> batteries have garnered increasing attention as efficient energy-storage systems due to their considerably high theoretical energy densities.<sup>10, 117-119</sup> In contrast to conventional batteries, metal- $O_2$  batteries feature an open cell structure so that the cathode material,  $O_2$ , can be obtained from the ambient atmosphere.<sup>120, 121</sup>

Metal-O<sub>2</sub> batteries exhibit high energy densities. For example, Li metal possesses a high theoretical specific energy (~3600 Wh kg<sup>-1</sup>), with a high cell voltage (nominally 2.96 V) in a Li-O<sub>2</sub> battery.<sup>11, 122</sup> Similarly, the Zn-O<sub>2</sub> system stands out for its high specific energy density (~1080 Wh kg<sup>-1</sup>) and volumetric energy density (~6100 Wh L<sup>-1</sup>) in aqueous electrolytes.<sup>11, 123</sup> However, the overall reactions of oxygen at the cathode in the rechargeable metal-O<sub>2</sub> batteries, known as the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), are often hindered by sluggish kinetics that lead to a decrease in both energy and power densities of the batteries.<sup>124, 125</sup> Therefore, the development of efficient bifunctional electrocatalysts for both ORR and OER is of great importance to enhance the performance of metal-O<sub>2</sub> batteries.

Generally, the noble metal-based materials, such as Pt,<sup>126, 127</sup> Pd,<sup>128, 129</sup> Ir<sup>130</sup> and Ru,<sup>131</sup> are highly efficient for electrocatalysis in metal-O<sub>2</sub> batteries, but practical applications are severely limited by their high cost and scarcity. Considerable efforts have also been devoted to the development of noble metal-free bifunctional electrocatalysts, such as the nitrogen-doped graphene and carbon nanotubes,<sup>25, 132,</sup> <sup>133</sup> first-row transition metal oxides,<sup>134</sup> perovskite oxides,<sup>135, 136</sup> and graphene composited catalysts.<sup>137, 138</sup>

The synthesis of the catalysts generally consists of two major approaches: wet chemistry methods such as hydro-/solvothermal reactions, and thermal annealing/pyrolysis processes. Recently, our group developed a facile method to produce porous graphene by direct laser writing on a polyimide (PI) sheet to produce laser-induced graphene (LIG).<sup>28</sup> LIG has high porosity, good electrical conductivity and chemical stability, all of which are conducive to the development of porous materials for efficient cathode catalysts.<sup>29, 30</sup> Based on this technique, we further develop approaches for the in situ formation of metal oxide/LIG composites for either OER or ORR.<sup>70, 95</sup> We present here a straightforward method for the syntheses of highly efficient bifunctional OER/ORR catalysts combining both advantages of the LIG and cobalt oxides. The catalyst is synthesized by one-step laser scribing on the precursor-loaded LIG/PI sheet that does not require any further liquid phase reactions, post thermal annealing or pyrolysis. The resultant Co<sub>3</sub>O<sub>4</sub>/LIG shows remarkably high OER/ORR activities, with performances comparable to the noble metal-based catalysts in alkaline electrolyte. Moreover, the  $Co_3O_4/LIG$  demonstrates high activity as the cathode material for both aprotic Li- $O_2$ and aqueous Zn-air batteries. The batteries exhibited low overpotentials in both charge and discharge processes with improved durability. This report regarding LIG-assisted synthesis of bifunctional catalysts in the solid phase might even be beneficial for the synthesis of other transition metal-based catalysts.

# 3.2. Laser-Induced Graphene with Bifunctional Catalysts for Metal-Oxygen Batteries

### 3.2.1. Experimental Section

#### 3.2.1.1. Material Synthesis

**Preparation of the catalyst.** All samples were prepared under ambient air following the similar procedures as reported in Chapter 4. Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser (10.6  $\mu$ m, Universal XLS10MWH laser cutter platform) on the PI film in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2 × 2 cm<sup>2</sup> structure.

1 M Co(NO<sub>3</sub>)<sub>2</sub> solution was prepared with deionized water. The as-prepared LIG (2 × 2 cm<sup>2</sup>) was treated by the O<sub>2</sub> plasma (Boekel Model 135500) for 1 min to increase the hydrophilicity. 80  $\mu$ L of the solution were dropped onto the LIG. The soaked LIG (on PI) was dried in air at room temperature overnight and then under vacuum (~120 mm Hg) for 6 h. Then the LIG was lased again atop the previous LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). Then the powder was scratched off from the PI and collected for further characterization. MnO<sub>x</sub>/LIG was prepared by the same procedures except that the solution was 1 M MnSO<sub>4</sub>.

#### 3.2.1.2. Material Characterization

**General characterization.** Scanning electron microscope (SEM) images were obtained by a FEI Quanta 400 high-resolution field emission SEM. Transmission electron microscopy (TEM) images were obtained by a JEOL 2100F field emission gun transmission electron microscope. X-ray photoelectron spectroscopy (XPS) was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. The XPS spectra were taken from the as-prepared catalysts on PI. Raman spectroscopy was performed at 532 nm laser excitation. ICP-OES was done by a Perkin Elmer Optima 8300 instrument. The material was digested by HNO<sub>3</sub>.

**Electrochemical measurements.** Electrochemical measurements were done on a rotating disk electrode (5 mm in diameter, Pine Research Instrumentation). For the preparation of the working electrode, 4 mg of the catalyst and 80 µl of 5 wt% Nafion solution were mixed in 1 mL water/ethanol (4/1, v/v) followed by 2 h bath sonication (Cole Parmer, model 08849-00) to form a homogeneous ink. Then 12 µL of the catalyst ink was dropped onto the glassy carbon electrode and dried under vacuum (~120 mm Hg) at room temperature (the loading is ~0.265 mg cm<sup>-2</sup>). The electrochemical measurements were carried out in a 3-electrode configuration using a CHI 608D electrochemical workstation. A Pt wire and a Hg/HgO electrode (in 1 M KOH) were used as the counter and reference electrodes, respectively. The tests were done in 0.1 M KOH with 95% iR compensation. For the OER test, the scan rate of working electrode was 5 mV s<sup>-1</sup> with a rotating speed of 1600 rpm. The number of electrons transferred (*n*) during ORR was calculated by the previously discussed Koutecký-Levich (K-L) equation according to the LSV curves with varying rotating speed from 225 to 1600 rpm.

**Battery test.** The electrochemical performance of Co<sub>3</sub>O<sub>4</sub>/LIG bifunctional catalysts was tested in lithium-oxygen cells through coin type CR2032 cells. All the cells were assembled in the glove box under argon atmosphere. The CR2032 lithium-oxygen cell includes the lithium foil, Celgard 2500 membrane, 0.5 M lithium bis(trifluoromethanesulfonyl)imide/tetraethylene dimethyl glycol ether (LiTFSI/TEGDME) with 0.05 M LiI and the air cathode electrode. The cathode was prepared by casting slurry which consists 80 wt% catalysts, 10 wt% (Super P, TIMCAL) and 10 wt% polyvinylidene difluoride (PVDF; Alfa Aesar) in N-methyl-2pyrrolidone (NMP) on a piece of carbon paper. The galvanostatic discharge/charge tests were carried out in voltage range of 2.0 to 4.3 V (vs Li/Li<sup>+</sup>). Pure O<sub>2</sub> flow was maintained during the test. The Co<sub>3</sub>O<sub>4</sub>/LIG cathode for rechargeable Zn-air battery was tested on a home-made device. The electrolyte is 6 M KOH with 0.2 M Zn(OAc)<sub>2</sub>. The cathode material was loaded on a carbon fiber paper ( $\sim 1 \text{ mg cm}^{-2}$ ), and a Zn plate was used as the anode. Pure O<sub>2</sub> flow was maintained during the test.

## 3.2.2. Result and Discussion

The Co<sub>3</sub>O<sub>4</sub>/LIG catalyst was prepared by a recently developed LIG-assisted method in the solid phase. As shown in **Figure 3.1**a, LIG was formed on a PI sheet followed by O<sub>2</sub> plasma treatment to enhance the hydrophilicity of the LIG. Then the

precursor aqueous solution, 1 M Co(NO<sub>3</sub>)<sub>2</sub>, was added to the LIG pattern. The porous LIG with enhanced wettability uniformly adsorbed the solution and therefore the metal salts were well-distributed in the LIG after the drying process. Subsequently, a second laser scribing was carried out atop the treated LIG. The nucleation of Co<sup>2+</sup> was triggered by the extremely high local temperature when the laser hit the LIG and resulted in the formation of the Co<sub>3</sub>O<sub>4</sub>/LIG catalyst.<sup>28</sup> In the previously reported synthesis of CoO<sub>x</sub>/LIG, the metal precursor was dissolved in the poly(amic acid), the PI precursor, and a pressurized thermal cycle of 250-300 °C was needed followed by a thermal annealing process at 750 °C.<sup>95</sup> The present method is not limited to the poly(amic acid) solubility of the metal precursor and it can all be done on the commercial PI film. Also, the resultant Co<sub>3</sub>O<sub>4</sub>/LIG is directly used as the cathode catalysts for metal-O<sub>2</sub> batteries without any post treatment.



Figure 3.1. Synthesis and characterization of Co<sub>3</sub>O<sub>4</sub>/LIG.

(a) Preparation of the Co<sub>3</sub>O<sub>4</sub>/LIG catalyst. (b) SEM and (c) TEM images of the Co<sub>3</sub>O<sub>4</sub>/LIG. The inset HRTEM image shows the lattice planes of Co<sub>3</sub>O<sub>4</sub> nanocrystals.

**Figure 3.1b** and **Figure 3.2** shows the scanning electron microscopy (SEM) images of the Co<sub>3</sub>O<sub>4</sub>/LIG at different magnifications. The Co<sub>3</sub>O<sub>4</sub>/LIG exhibits a highly porous surface morphology with much graphenic structure opening to the surface, which would contribute to a large active surface area<sup>28, 70</sup> to enable facile mass transport with the electrolyte during the electrochemical reactions. No large particles or aggregates were observed in the SEM images, suggesting a homogeneous distribution of the metal oxide particles in the LIG. The transmission electron microscopy (TEM) images shown in **Figure 3.1**c illustrate that the nanoparticles are embedded in the graphene with sizes of 5 to 10 nm. The nanocrystals in Co<sub>3</sub>O<sub>4</sub>/LIG display clear lattice fringes in the high-resolution TEM images. The Co<sub>3</sub>O<sub>4</sub> crystal phase planar spacing of the (220), (311) and (111) planes are 0.286, 0.242 and 0.480 nm, respectively.<sup>139</sup> The multilayer graphene structure is also evidenced by the characteristic interplanar spacing of 0.34 nm as shown in **Figure 3.3**.<sup>28</sup>



Figure 3.2. SEM images of the  $Co_3O_4/LIG$  at different magnifications.



### Figure 3.3. TEM images of the Co<sub>3</sub>O<sub>4</sub>/LIG.

The structure of Co<sub>3</sub>O<sub>4</sub>/LIG was further studied by Raman spectroscopy and X-ray diffraction (XRD). As shown in Figure 3.4a, the peaks at ~1585 and 2700 cm<sup>-1</sup> of the Raman spectrum correspond to the G and 2D peaks of graphene, respectively. The D band at 1342 cm<sup>-1</sup> is characteristic of bent graphene layers and defects.<sup>140</sup> The  $I_G/I_{2D}$  ratio is ~2.5, indicating the presence of a multilayer graphenic structure, which is consistent with the observation from the TEM images. The region circled by the dashed line in **Figure 3.4**a displays the Raman features of Co<sub>3</sub>O<sub>4</sub> as illustrated in **Figure 3.4**b. Two characteristic peaks at ~470 and 671 cm<sup>-1</sup> can be assigned to the  $E_g$  and  $A_{1g}$  modes of Co<sub>3</sub>O<sub>4</sub>.<sup>141</sup> The XRD spectra of Co<sub>3</sub>O<sub>4</sub>/LIG further confirmed the graphenic structure of LIG by a typical (002) peak of graphene at ~26° ( $d_{002} = 0.34$  nm). The (111), (311), (222) and (422) peaks from crystalline Co<sub>3</sub>O<sub>4</sub> were also observed.<sup>141</sup>

The amount of Co in the Co<sub>3</sub>O<sub>4</sub>/LIG was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The Co content is ~4.2 wt%. The chemical composition of the Co<sub>3</sub>O<sub>4</sub>/LIG was studied by X-ray photoelectron spectroscopy (XPS). The Co  $2p_{3/2}$  core level region consists of two main peaks at 780 and 782 eV, which indicate the presence of both +2 and +3 oxidation states of Co.<sup>142</sup> The C 1s spectrum, with a predominant peak centered at 284.5 eV, reveals the graphitic carbon in the catalyst. The O 1s spectrum further shows the C-O and C=O moieties on the LIG.<sup>29</sup>



Figure 3.4. Characterization of the Co<sub>3</sub>O<sub>4</sub>/LIG.

(a-b) Raman spectra of the catalyst, the dashed line indicates the Raman fingerprints of Co<sub>3</sub>O<sub>4</sub>. The Raman active modes are  $F_{2g}$  (191 cm<sup>-1</sup>, 511 cm<sup>-1</sup> and 610 cm<sup>-1</sup>),  $E_g$  (472 cm<sup>-1</sup>), and  $A_{1g}$  (678 cm<sup>-1</sup>). (c) Powder XRD pattern of the Co<sub>3</sub>O<sub>4</sub>/LIG. High-resolution XPS spectrum in (d) Co 2p and (e) C 1s and O 1s regions.



Figure 3.5. Electrochemical characterization of the Co<sub>3</sub>O<sub>4</sub>/LIG.

(a) CV curves of  $Co_3O_4/LIG$  and pristine LIG in  $O_2$ -saturated 0.1 M KOH at 1600 rpm. (b) OER polarization curves of  $Co_3O_4/LIG$  and pristine LIG at 1600 rpm; the inset shows the corresponding Tafel slope. (c) CV curves of  $Co_3O_4/LIG$  in Ar- and  $O_2$ -saturated 0.1 M KOH at a scan rate of 20 mV s<sup>-1</sup>. (d) LSV curves for ORR at different rotating speeds in  $O_2$ -saturated 0.1 M KOH.

The electrocatalytic activity of Co<sub>3</sub>O<sub>4</sub>/LIG was characterized using a rotating disk electrode in 0.1 M KOH electrolyte. The cyclic voltammetry (CV) curves in **Figure 3.5**a show the complete electrocatalytic reactions (ORR and OER) of

Co<sub>3</sub>O<sub>4</sub>/LIG and pristine LIG at 1600 rpm in O<sub>2</sub>-saturated electrolyte. The Co<sub>3</sub>O<sub>4</sub>/LIG exhibited significantly enhanced current density compared LIG in both OER and ORR despite the low content of the Co species. A pair of redox peaks was observed for Co<sub>3</sub>O<sub>4</sub>/LIG at ~1.1 V (*vs* RHE), which are attributed to the faradic reaction for Co-O/Co-OOH.<sup>143</sup> The OER kinetics were further investigated by linear swept voltammetry (LSV) as shown in **Figure 3.5**b. The Co<sub>3</sub>O<sub>4</sub>/LIG exhibited an onset potential of ~1.49 V, beyond which the current density increased rapidly with a low Tafel slope of 40 mV dec<sup>-1</sup>. The current density reached 10 mA cm<sup>-2</sup> at 340 mV overpotential. The electrochemical impedance spectra (**Figure 3.6**) also revealed the low charge transfer resistance of 25  $\Omega$  at 350 mV overpotential. Conversely, pristine LIG suffered from sluggish kinetics with a Tafel slope as high as 135 mV dec<sup>-1</sup>. While the catalyst system here is clearly very easy to prepare in a solvent-free manner, the OER performance of Co<sub>3</sub>O<sub>4</sub>/LIG is comparable or even better than the other Co-based OER catalysts that have been reported as summarized in **Table 3.1**.



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Catalyst	Preparation method	Onset E (V)	η <sub>10</sub> (mV)	Tafel slope (mV dec <sup>-1</sup> )
Co <sub>3</sub> O <sub>4</sub> /LIG	LIG	1.49	340	40
Co <sub>3</sub> O <sub>4</sub> /MCNT <sup>144</sup>	Hydrothermal	1.51	390	65
Co <sub>3</sub> O <sub>4</sub> /C nanowires <sup>145</sup>	Hydrothermal and thermal annealing 1.47		290	70
Au-meso-Co <sub>3</sub> O <sub>4</sub> <sup>146</sup>	Nanocasting 1.53 method		440	46
meso-Co <sub>3</sub> O <sub>4</sub> <sup>147</sup>	Template method	-	411	80
Hollow Ni-Co oxide <sup>148</sup>	NaBH <sub>4</sub> reduction	1.501	362	61.4
Mn <sub>x</sub> Co <sub>3-x</sub> O <sub>4-δ</sub> <sup>149</sup>	Self-templating 1.52		350	85
NiCo LDH nanosheets <sup>150</sup>	Solvothermal	1.52	420	113
ZnCo LDH/graphene <sup>151</sup>	Co-precipitation	1.56	430	73

# Figure 3.6. EIS of Co<sub>3</sub>O<sub>4</sub>/LIG at different OER overpotentials in 0.1 M KOH.

# Table 3.1. Comparison of the Co<sub>3</sub>O<sub>4</sub>/LIG catalysts with Co-based OER catalysts (in 0.1 M KOH).

**Figure 3.5**c displays the CV curves of  $Co_3O_4/LIG$  for ORR in Ar- and O<sub>2</sub>saturated electrolyte. Despite any disturbances caused by O<sub>2</sub> bubbling as seen by the small-peak riddled, the current density sharply increased with an  $E_{1/2}$  redox peaks of O<sub>2</sub>/OH<sup>-</sup> at 0.72 V, suggesting an efficient reduction of O<sub>2</sub> to OH<sup>-</sup>. The Co<sub>3</sub>O<sub>4</sub>/LIG showed an improved activity compared to LIG (**Figure 3.7**), and the low ORR Tafel slope of 70 mV dec<sup>-1</sup> (**Figure 3.8**) is comparable to those of graphene-based composites such as Fe-N-rGO (~110 mV dec<sup>-1</sup>)<sup>152</sup> and Co<sub>3</sub>O<sub>4</sub>/N-rmGO (~42 mV dec<sup>-1</sup>).<sup>137</sup> The ORR kinetics was further assessed by LSV at different rotating speeds. Linear fitting of the K-L plots reveals an electron-transfer number (*n*) of ~3.5 at the selected potentials (**Figure 3.8**b), demonstrating that the ORR by Co<sub>3</sub>O<sub>4</sub>/LIG is dominated by a four-electron transfer pathway (O<sub>2</sub> to OH<sup>-</sup>). The slight deviation of n from 4 might be caused by the carbon surfaces as observed for conductive carbon supported catalysts.<sup>68</sup>



Figure 3.7. LSV curves of Co<sub>3</sub>O<sub>4</sub>/LIG and LIG in O<sub>2</sub>-saturated 0.1 M KOH at 1600 rpm.



Figure 3.8. Supplementary ORR data for Co<sub>3</sub>O<sub>4</sub>/LIG.

(a) LSV curves of Co<sub>3</sub>O<sub>4</sub>/LIG for ORR, inset shows the Tafel slope. (b) K-L plots of Co<sub>3</sub>O<sub>4</sub>/LIG.

The bifunctional catalytic activity of Co<sub>3</sub>O<sub>4</sub>/LIG was characterized by the difference in potential between the selected OER current density (10 mA cm<sup>-2</sup>) and ORR current density (-3 mA cm<sup>-2</sup>). The values are summarized in **Table 3.2**.The *E*OER-*E*ORR of Co<sub>3</sub>O<sub>4</sub>/LIG is 0.98 V, which is slightly higher than that of Ir/C (0.92 V), but still remarkably lower than that of Pt/C (1.16 V) and Ru/C (1.01 V).<sup>153</sup> In addition, the Co<sub>3</sub>O<sub>4</sub>/LIG shows higher bifunctional activity than the Co- and Mn-based catalysts prepared by hydrothermal reaction or electrodeposition (**Table 3.2**). The smaller the value is, the lower the overpotential that is required to reach a specific current for either OER or ORR, which is essential to lower the overpotential for charge and discharge process in metal-O<sub>2</sub> batteries.

Catalyst	Preparation method <sup>a</sup>	<i>E</i> <sub>ORR</sub> (V) at -3 mA cm <sup>-2</sup>	<i>Е</i> оек (V) at 10 mA cm <sup>-2</sup>	Eoer-Eorr (V)
Co3O4/LIG	LIG	0.59	1.57	0.98
20 wt% Ir/C <sup>153</sup>	-	0.69	1.61	0.92
20 wt% Pt/C <sup>153</sup>	-	0.86	2.02	1.16
20 wt% Ru/C <sup>153</sup>	-	0.61	1.62	1.01
Co <sub>3</sub> O <sub>4</sub> <sup>154</sup>	НТ	0.61	1.74	1.13
Co(OH)2 <sup>154</sup>	HT	0.66	1.68	1.02
NiCo <sub>2</sub> O <sub>4</sub> /G <sup>155</sup>	HT	0.54	1.67	1.13
Mn oxide <sup>153</sup>	ED	0.73	1.77	1.04

Table 3.2. Comparison of the  $Co_3O_4/LIG$  catalysts with recently reported OER/ORR bifunctional catalysts.

<sup>a</sup>Abbreviation: HT: hydrothermal reaction; ED: electrodeposition.



Figure 3.9. Zn-air battery with Co<sub>3</sub>O<sub>4</sub>/LIG as the cathode catalyst.

(a) Open-circuit voltage and (b) the power density and charge/discharge polarization plots. The galvanostatic discharge and charge cycling curves of the rechargeable battery at (c) 2 mA cm<sup>-2</sup> and (d) 10 mA cm<sup>-2</sup>. (e) Long-term cycling performance of the battery at 10 mA cm<sup>-2</sup> (600 s per cycle).



Figure 3.10. Discharge polarization curve and corresponding power density up to 100 mA cm<sup>-2</sup>.

In consideration of the excellent bifunctionality of Co<sub>3</sub>O<sub>4</sub>/LIG, we fabricated a homemade Zn-air battery using the gas diffusion layer (carbon fiber paper, CFP) loaded with catalysts (1 mg cm<sup>-2</sup>) for the cathode, with a Zn plate as the anode and 0.2 M Zn(OAc)<sub>2</sub> in 6 M KOH as the electrolyte. The battery exhibited a high opencircuit voltage of 1.46 V (**Figure 3.9**). **Figure 3.9**b displays the charge and discharge polarization curves with the corresponding power density. The power density reached 47.6 mW cm<sup>-2</sup> at 50 mA cm<sup>-2</sup>, and further reached 84.2 mW cm<sup>-2</sup> at 100 mA cm<sup>-2</sup> (**Figure 3.10**). An ideal bifunctional catalyst should possess high discharge voltage, low charge voltage and reversibility. **Figure 3.9**c and **Figure 3.9**d show the galvanostatic charge/discharge profile at 2 and 10 mA cm<sup>-2</sup>, respectively. The battery showed a remarkably stable charging voltage of 2.01 V and a discharge voltage of 1.24 V at 2 mA cm<sup>-2</sup>. The voltage gap between charge and discharge increased to 0.96 V at 10 mA cm<sup>-2</sup>. The Zn-air battery also exhibited very good cycling stability as **shown** in **Figure 3.9**e. The voltage gap slightly increased by ~180 mV after 400 cycles. Therefore, the Co<sub>3</sub>O<sub>4</sub>/LIG has shown promising applicability as the cathode for Zn-air batteries with a high round-trip efficiency and notable stability.



Figure 3.11. Characterization of the Co<sub>3</sub>O<sub>4</sub>/LIG cathode in Li-O<sub>2</sub> battery.

(a) Galvanostatic cycling performance of the Co<sub>3</sub>O<sub>4</sub>/LIG electrode at a current density of 0.08 mA cm<sup>-2</sup> with limited capacity of 430 mAh g<sup>-1</sup>; (b) first discharge and charge profile of the cyclic performance; (c) discharge capacity

and terminal voltage versus cycle number; (d) charge capacity and terminal voltage versus cycle number.

The electrocatalytic activity of  $Co_3O_4/LIG$  was further examined in Li-O<sub>2</sub> batteries using coin cell architecture with 0.5 М lithium а bis(trifluoromethanesulfonyl)imide (LiTFSI) and in 0.05 M LiI in tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte. Figure 3.11a shows the galvanostatic charge/discharge profile of the cell in the first 100 cycles with a cut-off capacity of 430 mAh g<sup>-1</sup>. The voltage gap of the charge/discharge process at the 1<sup>st</sup> cycle was as low as 0.42 V (**Figure 3.11**b). The discharge voltage of Co<sub>3</sub>O<sub>4</sub>/LIG cell was  $\sim 2.73$  V (vs Li<sup>+</sup>/Li) in the 1<sup>st</sup> cycle and slightly decreased to  $\sim 2.67$  V in the 100<sup>th</sup> cycle; both were close to the theoretical discharge voltage (2.96 V), suggesting a stable energy output of the cell.<sup>156</sup>

The Li-O<sub>2</sub> battery exhibited outstanding cycle stability as shown in **Figure 3.11**and **Figure 3.11**d. The charge/discharge terminal voltage and capacity (within 2.0 to 4.3 V) were plotted against the cycle number. The discharge capacity reached 430 mAh g<sup>-1</sup> for 242 cycles with a slightly decreased discharge terminal voltage from 2.73 V to 2.40 V of the 242<sup>nd</sup> cycle. Similarly, the charge terminal voltage increased to 3.73 V at 100<sup>th</sup> cycle and further to 4.3V at 242<sup>nd</sup> cycle. The rapid decrease of capacity starting at the ~245<sup>st</sup> cycle together with the significant increase of the overpotentials might be caused by several factors, such as the electrolyte drying out and/or the cathode becoming covered by insulating

byproducts. In comparison, the pristine CFP current collector showed poor cyclability of up to 20 cycles in the same voltage window (**Figure 3.12**). The charge/discharge terminal voltage increased/decreased rapidly within the first few cycles. Therefore, the capacity from the current collector was negligible since the Co<sub>3</sub>O<sub>4</sub>/LIG possessed much higher activity. It is worth noting that the Co<sub>3</sub>O<sub>4</sub>/LIG also showed remarkable stability in air. **Figure 3.13** illustrates the cycle stability of the battery working in purified air (CO<sub>2</sub> and moisture removed by filtration) for up to 98 cycles. Because of the low overpotential of the Co<sub>3</sub>O<sub>4</sub>/LG electrode, the decomposition of the electrolyte and oxidation of carbon support was minimized, resulting in a long battery cycle life.<sup>157</sup>



Figure 3.12. Galvanostatic cycling performance of an CFP electrode at a current density of 0.08 mA cm<sup>-2</sup>.



Figure 3.13. Galvanostatic cycling performance of the Co<sub>3</sub>O<sub>4</sub>/LIG Li-O<sub>2</sub> battery in purified air (moisture and CO<sub>2</sub> removed by filter).

The electrochemical reaction of O<sub>2</sub> in the cell was investigated by CV in Ar and O<sub>2</sub> atmosphere. **Figure 3.14**a displays the data recorded between 2.0 and 4.5 V with a scan rate of 0.5 mV s<sup>-1</sup> obtained after 1<sup>st</sup> cycle. In Ar, the current density was very low and did not show any significant peak. Both the cathodic and anodic currents increased in O<sub>2</sub> atmosphere, indicating the ORR of O<sub>2</sub> and the OER of the Li<sub>2</sub>O<sub>2</sub>, respectively. The ORR onset is ~2.77 V, very close to 2.96 V, suggesting the high inherent oxygen reduction activity of Co<sub>3</sub>O<sub>4</sub>/LIG. The OER onset potential is ~3.15 V, but the overpotentials for both ORR and OER slightly increase as the cell cycles due to the formation of byproducts and incomplete decomposition of discharge products.<sup>69</sup> The electrochemical impedance spectra (EIS) were also measured to study the intrinsic behavior of the Li-O<sub>2</sub> battery during cycling. **Figure 3.14**b shows the EIS recorded at the initial stage and the end of first discharge/charge process under open circuit voltage. The equivalent serial resistance remained nearly the same, however, the charge transfer resistance increased from ~200  $\Omega$  to ~450  $\Omega$ . This increase in the interfacial resistance might be caused by the poor electrically conductive products at the electrode/electrolyte interface, which remains a typical hurdle for current Li-O<sub>2</sub> batteries.<sup>69</sup> The LIG-assisted method also works well for the preparation of bifunctional catalysts based on other transition metals in addition to Co, for example, Mn. **Figure 3.15** shows the XPS and cycling performance for MnO<sub>x</sub>/LIG in a Li-O<sub>2</sub> battery. Although the performance was not as high as in the Co<sub>3</sub>O<sub>4</sub>/LIG, the MnO<sub>x</sub>/LIG cathode showed considerable stability for ~100 cycles.



Figure 3.14. Electrochemical analysis of the Li-O<sub>2</sub> battery.





Figure 3.15. MnO<sub>x</sub>/LIG cathode for Li-O<sub>2</sub> battery.

(a) XPS spectrum of  $MnO_x/LIG$  and the cycling performance of  $MnO_x/LIG$  as the cathode for Li-O<sub>2</sub> battery in (b) O<sub>2</sub> and (c) purified air.

#### 3.2.3. Conclusion

In this study, we demonstrated the solid phase synthesis of an OER/ORR bifunctional catalyst, Co<sub>3</sub>O<sub>4</sub>/LIG, through a facile LIG-based process. Benefiting from the high porosity and conductivity of LIG with the intrinsic high activity of Co<sub>3</sub>O<sub>4</sub>, the Co<sub>3</sub>O<sub>4</sub>/LIG exhibited high activity for OER and ORR in alkaline media. These favorable properties further led to the enhancement performance of Co<sub>3</sub>O<sub>4</sub>/LIG as a cathode material for metal-air batteries. The Co<sub>3</sub>O<sub>4</sub>/LIG worked well as an efficient cathode material for the aqueous Zn-air battery as well as the aprotic Li-O<sub>2</sub> battery. The batteries showed low overpotentials in both charge and discharge processes combined with excellent cycling durability. In addition to the notable catalytic performance of Co<sub>3</sub>O<sub>4</sub>/LIG, the facile synthetic method brings about a new way for the design and synthesis of bifunctional and multifunctional catalysts. This contribution is expected to encourage further development in the carbon-metal oxide composited cathodes for metal-air batteries using the LIG approach.

## **3.3. Experimental Contributions**

**Muqing Ren** designed the experiments and conducted part of the characterizations including SEM, XPS, TEM, XRD, OER, ORR and battery test. Jibo Zhang designed part of the experiments, prepared the samples, and conducted part of the characterizations including Raman, XPS, ICP-OES, electrochemical measurements.

Chapter 4

# Laser-Induced Graphene Hybrid Catalysts for Rechargeable Zn-Air Batteries

This chapter was entirely copied from reference 158.

# 4.1. Introduction

Rechargeable Zn-air batteries are projected to be key players in serving the increasing demand for high-performance electrical energy storage and conversion systems.<sup>11, 123, 159</sup> Zn-air batteries benefit from several potential advantages such as high theoretical energy density of 1218 Wh kg<sup>-1</sup> (6136 Wh L<sup>-1</sup>), low cost and improved safety.<sup>160</sup> However, the large-scale development of Zn-air batteries is hindered by the poor performance in rechargeability, power density and energy efficiency. All of these performance problems originate from the fundamental

chemical behavior in the air cathode that results in the sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).<sup>12, 160</sup> Noblemetal catalysts such as Pt,<sup>161, 162</sup> Ru<sup>163</sup>, Ir<sup>164</sup> and their derivatives,<sup>165</sup> have shown high activity in the oxygen electrocatalysis. However, their scarcity, high cost and poor durability have limited their widespread use. The pursuit of earth-abundant and low-cost electrocatalysts has led to increasing research in the field.<sup>166, 167</sup> For example, transition metal oxides,<sup>134, 168</sup> sulfides<sup>169-171</sup> and heteroatom-doped carbon materials<sup>172, 173</sup> have shown promising performance with activities comparable to those of the noble-metal catalysts. However, the present synthetic methods to obtain the catalysts are primarily based on wet chemistry and thermal pyrolysis. For example, the direct carbonization of precursors (*e.g.* metal-organic-frameworks) at high temperature,<sup>26, 145, 174</sup> hydrothermal reactions,<sup>137, 175</sup> and a combination of wet chemistry and thermal treatments have been used to prepare the catalysts. Either the precursors or the method itself could increase the complexity and cost for large scale production. A straightforward and simple method that is free of complex and high cost procedures would be beneficial to the continued development of the field.

Here, we present the facile synthesis of ternary metal oxide/graphene hybrid materials by using a laser-based technique to produce efficient cathode catalysts for rechargeable Zn-air batteries. Laser-induced graphene (LIG) is the porous graphene grown by direct laser writing on a polyimide (PI) sheet.<sup>28, 176</sup> The laser systems used are commonly found in machine shops and the formation is easily conducted in the open air without exogenous gases or furnaces, paving the way for roll-to-roll

processing routes. This technique has been further developed for the synthesis of metal oxide nanoparticle/graphene composites through a re-lasing process.<sup>70, 95, 114</sup> The previous method<sup>95</sup> synthesized the metal oxide/LIG composite by doping the metal salts into the PI precursor (polyamic acid, PA). The laser scribing of the doped PA simultaneously induces the carbonization of the PA and the nucleation of metal ions. However, it requires that the metal salts be soluble and compatible with the PA. In addition, the process takes several days to complete. The present method is a re-lasing process and does not have the requirement of metal salt solubility and compatibility in PA. Additionally, the catalysts prepared by the previous method did not exhibit good ORR activity unless treated at 750 °C for 30 min. Conversely, the present method is a CVD-free approach and the resultant catalysts exhibit good activities for both OER and ORR.

In this study, four ternary metal oxide/LIG hybrid materials with different elemental composition, LIG-CoNiFe-1, LIG-CoNiFe-2, LIG-MnNiFe-1, and LIG-MnNiFe-2, were synthesized through the facile LIG method without any wet chemistry or thermal pyrolysis treatments. The elemental composition of the metal species is easily tuned in precursor solutions. The hybrid catalysts exhibited high activities toward ORR and OER in alkaline electrolyte that promoted their performance in rechargeable Zn-air batteries. The best catalyst, LIG-MnNiFe-1, demonstrates a maximum power density of 98.9 mW cm<sup>-2</sup>, a small overpotential of 0.88 V, a high energy density of >840 Wh kg<sup>-1</sup>, and excellent cycling stability for >500 cycles, outperforming the catalysts prepared using conventional wet and

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thermal methods. We further demonstrate the use of the all-LIG-derived materials

for development of flexible Zn-air batteries and water splitting systems.

# 4.2. Laser-Induced Graphene Hybrid Catalysts for Rechargeable Zn-Air Batteries

## 4.2.1. Experimental Section

## 4.2.1.1. Material Synthesis

**Preparation of the catalysts.** All samples were prepared under room temperature and ambient air. Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser cutter system (10.6  $\mu$ m, Universal XLS10MWH laser cutter platform) on the PI film in air using 3% of full power and 5% of full speed. The preparation of the catalysts followed a previously reported method.<sup>70</sup> 1 M Co(NO<sub>3</sub>)<sub>2</sub>, 1 M MnSO<sub>4</sub>, 1 M Ni(NO<sub>3</sub>)<sub>2</sub> and 1 M Fe(NO<sub>3</sub>)<sub>3</sub> solutions were prepared with deionized water. Then the solutions with different molar ratios were prepared with the total concentration of metal cations kept at 1 M. The as-prepared LIG (2 × 2 cm<sup>2</sup>) was treated by O<sub>2</sub> plasma (Model 1020 Plasma Cleaner, Fischione Instruments) for 5 min to increase the wettability of LIG with the precursor solutions. 80  $\mu$ L of the solutions were dropped uniformly onto the LIG. The soaked LIG (on PI) was dried under vacuum (~120 mm Hg) for 6 h. The LIG was lased again atop the previous LIG pattern under the same

conditions (3% of full power and 5% of full speed with an image density of 6). The powder was scratched off the PI using a spatula and collected for characterization. The MnNiFe/CFP was prepared by following a reported method.<sup>70</sup> Briefly, 80  $\mu$ L of the precursor solution was dropped onto the O<sub>2</sub> plasma treated (1 min) carbon fiber paper (CFP). Then the CFP was dried in a vacuum chamber (~120 mm Hg) overnight. The CFP was scribed by the laser beam with 3% of full power, 5% of full speed and an image density of 6. The area of the lased pattern was 10 × 10 mm<sup>2</sup>.

### 4.2.1.2. Materials characterization

**Materials characterization.** SEM images were obtained on a FEI Quanta 400 high-resolution field emission SEM. TEM images were obtained by a JEOL 2100F field emission gun transmission electron microscope. XPS was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. Raman spectroscopy was performed at 532 nm laser excitation.

**Electrochemical measurements.** For preparation of the working electrode, 4 mg of the catalyst and 80  $\mu$ L of 5 wt% Nafion solution were mixed in 1 mL water/ethanol (1/1, v/v) followed by 4 h bath sonication to form a homogeneous ink. 12  $\mu$ L of the ink was loaded onto a rotating disk electrode (RDE, glassy carbon, 5 mm in diameter), and dried in air at room temperature. The mass loading of the catalyst is ~0.22 mg cm<sup>-2</sup>. The electrochemical measurements were carried out in a 3-electrode configuration using a CHI 608D electrochemical workstation. Pt wire

and Hg/HgO (in 1 M KOH) were used as the counter and reference electrodes, respectively. The OER tests were done on the RDE at 1600 rpm in 0.1 M KOH with 95% iR compensation. The potential is normalized with RHE. The ORR tests were done in 0.1 M KOH with 95% iR compensation. O<sub>2</sub> bubbling into the electrolyte was maintained throughout the measurement to ensure continuous O<sub>2</sub> saturation. The number of electrons transferred (*n*) during ORR was calculated by Koutecky-Levich (K-L) eq according to the LSV curves with varying rotating speed from 225 to 1600 rpm.

**Zn-air battery test.** The air cathode was prepared by casting the catalyst ink on a gas diffusion layer (AvCarb P75T, FuelCellStore) at a mass loading of 1 mg cm<sup>-2</sup>. The Zn-air battery cathode was tested in a two-electrode configuration on a homemade device with a Zn plate as the anode. The electrolyte was 6 M KOH with 0.2 M Zn(OAc)<sub>2</sub>. All the tests were done in ambient air. The galvanostatic cycling tests of the batteries were conducted at 10 mA cm<sup>-2</sup> with 5 min discharge and 5 min charge, respectively. Pt/C and RuO<sub>2</sub> (Sigma-Aldrich) were mixed at 1:1 mass ratio and used for comparison.

For the flexible Zn-air battery fabrication, a PI film and a holey PI film (2 mm in diameter) were used as the substrate and top protection layer, respectively. The catalyst was loaded on carbon cloth (Plain carbon cloth, FuelCellStore) as the air cathode with a mass loading of 1 mg cm<sup>-2</sup>. A piece of Zn foil was used as the anode. For the preparation of the gel electrolyte membrane, 1 g PVA (MW 89000-98000 Aldrich) and 0.1 g PEO (MW 35000, Polysciences) were dissolved in 10 mL DI water

at 95 °C under stirring. 1 mL of 18 M KOH solution was added to the above solution, and the electrolyte was kept stirring at 95 °C for 30 min. The electrolyte solution was kept in a refrigerator for 12 h for solidification. Kapton tape was used to seal the edges. A nickel strip was used as the conductive lead.

A NTE30106 dual-color LED was used for demonstration. The catalytic LIG electrodes, LIG-Co-P and LIG-NiFe were fabricated by electrodeposition in a 3-three electrode configuration, with Ag/AgCl as the reference electrode and a Pt plate as the counter electrode. For the fabrication of LIG-Co-P, the electrolyte bath contained 50 mM CoCl<sub>2</sub>, 0.5 M NaH<sub>2</sub>PO<sub>2</sub>, and 0.1 M NaOAc. The deposition was done by consecutive linear scans between -0.3 and -1.0 V (*vs* Ag/AgCl) at a scan rate of 5 mV s<sup>-1</sup> for 10 cycles. For the fabrication of LIG-NiFe, the electrolyte bath contained 3 mM Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 3 mM Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The deposition was done at a constant potential of -1.0 V (*vs* Ag/AgCl) at room temperature. The optimized deposition time was 150 s.



Figure 4.1. (a) Schematic fabrication process of the catalysts and SEM images of (b) LIG-CoNiFe-1, (c) LIG-CoNiFe-2, (d) LIG-MnNiFe-1 and (e) LIG-MnNiFe-2. The scale bars are 5  $\mu$ m.

The synthesis of ternary metal oxide/graphene hybrid materials was done by the recently developed LIG method.<sup>70</sup> As depicted in **Figure 4.1a**, the materials were prepared *in situ* by laser scribing on the LIG loaded with metal salts. In the previous study, the Co oxide derived catalyst demonstrated a good ORR/OER bifunctionality as the cathode catalyst in a Zn-air battery.<sup>114</sup> However, the relatively low activity of Co in OER resulted in a charge potential higher than 2.1 V at 10 mA cm<sup>-2</sup>. A high charge potential in the Zn-air battery will lead to not only a low round-trip efficiency, but also the potential oxidation of the ORR active sites under anodic conditions and/or the corrosion of air cathode. In order to further lower the overpotentials in OER, we combined the high OER activity from NiFe-based catalysts<sup>83, 84</sup> with the ORR activity from the Co/Mn species<sup>177, 178</sup> to prepare the four ternary metal oxide/LIG hybrid catalysts. The Ni:Fe feed ratio of 1:1 is based on the optimized OER performance as reported.<sup>70</sup> LIG-CoNiFe-1 and LIG-CoNiFe-2 are prepared with atomic ratios (Co:Ni:Fe) of 1:1:1 and 3:1:1 in the precursor solutions, respectively. Similarly, LIG-MnNiFe-1 and LIG-MnNiFe-2 are prepared with atomic ratios (Mn:Ni:Fe) of 1:1:1 and 3:1:1 in the precursor solutions. The scanning electron microscopy (SEM) images shown in **Figure 4.1** illustrate the porous structure of the catalysts that contributes to good contact with the electrolyte. No large aggregates of particles were observed, indicating the uniform distribution of ternary metal oxides which are spontaneously formed in a well interconnected matrix of LIG. No further processing is needed. The porous LIG structure provided a conductive scaffold and to maximize the exposure of the surface active sites.



Figure 4.2. TEM images of (a) LIG-CoNiFe-1, (b) LIG-CoNiFe-2, (c) LIG-MnNiFe-1 and (d) LIG-MnNiFe-2. The TEM elemental mapping of (e) LIG-CoNiFe-2 and (f) LIG-MnNiFe-1. The scale bar is 10 nm for (a-d), and 100 nm for (e, f).


Figure 4.3. TEM images of (a) LIG-CoNiFe-1, (b) LIG-CoNiFe-2, (c) LIG-MnNiFe-1 and (d) LIG-MnNiFe-2. The scale bar is 20 nm. (e) The size distribution of nanoparticles in LIG-MnNiFe-1.



Figure 4.4. TEM elemental mapping of LIG-CoNiFe-1 and LIG-MnNiFe-2.

The transmission electron microscopy (TEM) images illustrate the nanoparticle/multi-layer graphene hybrid structure. As shown in **Figure 4.2**a-d and **Figure 4.3**, the metal oxide nanoparticles were embedded on and within graphene with a diameter of 5-10 nm. The TEM elemental mapping images (**Figure 4.2**e-f, **Figure 4.4**) further reveal the overlapping distribution of the metal species in the ternary metal oxides, suggesting the hybrid nature of the nanoparticles. The hybrid structure is also revealed by the power XRD diffraction pattern (**Figure 4.6**). The clearly identified D (~1340 cm<sup>-1</sup>), G (~1580 cm<sup>-1</sup>) and 2D (~2675 cm<sup>-1</sup>) peaks in the Raman spectra (**Figure 4.5**) confirm the existence of defective or bent graphenic structure that is the characteristic sign of LIG,<sup>28, 176</sup> and consistent with the observations from TEM images. The high D/G ratio of ~1.1 indicates the defects and

observations from TEM images. The high D/G ratio of ~1.1 indicates the defects and bent structures. Because LIG is formed through a rapid heating and cooling lasing process, it leads to the formation of more 5,7-membered rings<sup>28</sup> when compared to the CVD-grown thermodynamically stable graphene. Therefore, LIG is referred to as kinetic graphene. The G/2D ratio is ~1.8 through the catalysts, suggesting the multilayer structure of the graphene.



Figure 4.5. Spectral charaterizations of the catalysts.

(a) Raman spectra of the catalysts. The high-resolution XPS spectra in (b) C 1s,(c) Co 2p, (d) Mn 2p, (e) Ni 2p and (f) Fe 2p regions.



Figure 4.6. Powder XRD diffraction pattern of the catalysts.

# The symbols indicate the diffraction peaks from LIG (multilayer graphene), $NiO_x$ and $CoO_x$ .

The elemental compositions of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) as shown in **Figure 4.5.** The C 1s spectra show a characteristic peak of LIG at 284.5 eV, corresponding to the sp<sup>2</sup> carbon from graphene.<sup>179</sup> The Co species in LIG-CoNiFe-1 and LIG-CoNiFe-2 exist in +3 and +2 oxidation states as demonstrated by the 2p<sub>3/2</sub> peaks at 780.6 and 782.7 eV, respectively.<sup>180</sup> The satellite peaks might also bear the contributions from Fe Auger

signals. The Mn species in LIG-MnNiFe-1 and LIG-MnNiFe-2 exhibit a well-resolved spin-orbit splitting of 11.7 eV between  $2p_{2/3}$  (641.8 eV) and  $2p_{1/2}$  (653.5 eV), indicating the +4 oxidation state of Mn.<sup>181</sup> The Ni and Fe species are in +2 (Ni  $2p_{3/2}$  856.1 eV) and +3 (Fe  $2p_{3/2}$  711.1 eV) states, respectively.<sup>182</sup> The relative compositions of metal species in the catalysts have been summarized in

**Table 4.1**, all of which agree well with the feed ratio in the precursor solutions,suggesting the efficient consistency of the LIG method.

Catalyst	Co (%)	Mn (%)	Ni (%)	Fe (%)
LIG-CoNiFe-1	36	-	34	30
LIG-CoNiFe-2	56	-	20	24
LIG-MnNiFe-1	-	34	34	33
LIG-MnNiFe-2	-	57	20	23

 Table 4.1. Relative composition of the metal species in catalysts.

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Figure 4.7. ORR performance of ORR LIG-CoO<sub>x</sub> and LIG-MnO<sub>x</sub>.

LSV curves of (a) LIG-CoO<sub>x</sub> and (b) LIG-MnO<sub>x</sub> in O<sub>2</sub> saturated 0.1 M KOH. And the corresponding *n* calculated from K-L equation in (c) for LIG-CoO<sub>x</sub> and (d) for LIG-MnO<sub>x</sub>.



Figure 4.8 OER performance of LIG-CoO<sub>x</sub>, LIG-MnO<sub>x</sub> and LIG-NiFe.

(a) OER LSV curves of LIG-CoO<sub>x</sub>, LIG-MnO<sub>x</sub> and LIG-NiFe and (b) the calculated Tafel plots. (c) ORR LSV curves of LIG-NiFe and in O<sub>2</sub> saturated 0.1 M KOH and (d) the corresponding *n* calculated from K-L equation.



Figure 4.9. Electrochemical performance of the catalysts in 0.1 M KOH.

(a) OER polarization curves and (b) the corresponding Tafel plots. (c) ORR polarization curves in O<sub>2</sub>-saturated 0.1 M KOH at 1600 rpm. (d) ORR LSV curves of LIG-MnNiFe-1 at different rotating speeds. (e) Calculated *n* values at

### different potentials. (f) The E<sub>OER</sub> (j = 10 mA cm<sup>-2</sup>) and E<sub>ORR</sub> (j = -3 mA cm<sup>-2</sup>) values of the catalyst.

The electrochemical performance of the catalysts was assessed using a rotating disk electrode in 0.1 M KOH. As discussed above, Co- and Mn-based catalysts has shown promising activity for ORR, such as high onset potential and electron transfer number (*n*) of  $\sim 4$  (**Figure 4.7**). However, their OER activity is limited by the high onset potentials and Tafel slopes. On the contrary, NiFe oxide possess remarkably high OER activity but suffers from a poor ORR performance, specifically in terms of the *n* value (Figure 4.8). The ternary metal oxide/LIG catalysts are expected to exhibit high ORR/OER bifunctionality from the hybrid compositions. Figure 4 Figure 4.9a shows the linear sweep voltammetry (LSV) curves for OER at 1600 rpm, where all four hybrid catalysts exhibited lower onset potential than that of LIG-CoO<sub>x</sub> with similar Tafel slopes as that of LIG-NiFe. The incorporation of NiFe significantly enhances the OER performance. The OER activity is further quantitatively characterized by the potential to reach 10 mA cm<sup>-2</sup> (E<sub>OER</sub> value) as summarized in **Table 4.2**. The E<sub>OER</sub> values of the ternary metal oxide/LIG catalysts are significantly lower than that of LIG-CoO<sub>x</sub> and LIG-MnO<sub>x</sub>. LIG-CoNiFe-1 exhibited the lowest E<sub>OER</sub> value of 1.517 V (vs RHE). The E<sub>OER</sub> value of Mn-based catalyst was lowered from 1.850 V of LIG-MnO<sub>x</sub> to 1.543 V of LIG-MnNiFe-1. The ternary metal oxide/LIG materials have demonstrated OER activity comparable to the conventionally prepared catalysts (Table 4.3). It should be noted that the

characteristic anodic peak from Ni<sup>2+</sup> oxidation (**Figure 4.8a, b**) was not observed from the ternary metal oxide catalysts. This finding confirms the hybrid nature of the oxides since the high valence ions (Co<sup>3+</sup> or Mn<sup>4+</sup>) would suppress the oxidation of Ni<sup>2+</sup> and it is suggestive of the intrinsic synergetic effect between the metal species.<sup>103, 183</sup> The redox peak observed at ~1.4 V originates from the redox of Ni<sup>2+</sup> and Ni<sup>3+,4+</sup> under anodic conditions. Although the underlying mechanism is still under debate, recent studies have demonstrated that the presence of high valence metal ions (Fe<sup>3+</sup>, Co<sup>3+</sup> and Mn<sup>4+</sup>) suppress the oxidation of Ni<sup>2+</sup> to higher oxidation states.<sup>107</sup> The possible reasons may be the decreased affinity of oxygen for the Ni surface and destabilization of the Ni<sup>3+</sup> species due to the partial charge transfer from Ni to the high valence metal ions. In this manuscript, the relative molar ratio of Mn/Co+Fe to Ni is 2:1 and 4:1. Such high amounts of high valence metal ions would significantly suppress the redox of Ni, which is consistent with the literature<sup>103,105</sup> and our previous observation.<sup>70</sup>



Figure 4.10. ORR LSV curves of (a) LIG-CoNiFe-1, (b) LIG-CoNiFe-2 and (c) LIG-MnNiFe-2.



Figure 4.11. ORR K-L curves of (a) LIG-CoNiFe-1, (b) LIG-CoNiFe-2, (c) LIG-MnNiFe-1 and (d) LIG-MnNiFe-2.

At the same time, the ternary metal oxide/LIG catalysts shows promising ORR activity as inherited from the Co/Mn species. The ORR LSV curves at 1600 rpm were obtained in O<sub>2</sub>-saturated electrolyte as illustrated in **Figure 4.9c**. LIG-MnNiFe-2 delivers the highest limiting current of -4.62 mA cm<sup>-2</sup>, followed by -4.53 mA cm<sup>-2</sup> of LIG-MnNiFe-1. The current densities of LIG-CoNiFe-1 and LIG-CoNiFe-2 are slightly lower than the former two catalysts. The linearly fitted Koutecky-Levich (K-L) plots were performed on the ORR LSV curves recorded at various electrode-rotation

speeds from 225 to 1600 rpm (Figure 4.9d, Figure 4.10 and Figure 4.11) to examine the ORR kinetic performance. The parallel lines fitted at different potentials indicate the first-order reaction kinetics with respect to the dissolved O<sub>2</sub> concentration. As shown in **Figure 4.9e**, the catalysts show *n* values ranging from 3.2-4.0, indicating the existence of direct four-electron reaction pathways. However, for LIG-CoNiFe-1 and LIG-CoNiFe-2, the *n* values are  $\sim$ 3.2-3.6 and  $\sim$ 3.5-3.8, respectively; a significant deviation of n from 4.0 indicating the non-negligible formation of HO<sub>2</sub><sup>-</sup> through the two-electron pathway. This could be caused by either the competing sites from NiFe or the LIG matrices.<sup>184</sup> In contrast, the LIG-MnNiFe-1 and LIG-MnNiFe-2 possess *n* values of  $\sim$ 4.0 that originates from the intrinsic high activity of Mn.<sup>185</sup> The overall bifunctional activity is evaluated by the potential difference between EOER and EORR (Figure 4.9f and Table 4.2). The highest activity was achieved on LIG-MnNiFe-1 (0.974 V), which also exhibits a considerably good n value of  $\sim$ 3.8-4.0. Although Co species contribute to a higher OER activity, the Mn species lead to a more balanced OER/ORR bifunctionality of the ternary metal oxide. And therefore LIG-MnNiFe-1 and LIG-MnNiFe-2 are promising candidates for the cathode catalysts in Zn-air batteries.

Catalyst	Eorr (V) <sup>a</sup>	Eoer (V) <sup>b</sup>	n	Eoer- Eorr (V)
LIG-NiFe	0.560	1.520	~2.5-3.5	-
LIG-CoO <sub>x</sub>	0.571	1.575	~3.5	1.004
LIG-MnO <sub>x</sub>	0.622	1.850	~3.9-4.0	1.228
LIG-CoNiFe-1	0.450	1.517	~3.2-3.6	1.067
LIG-CoNiFe-2	0.546	1.529	~3.5-3.8	0.983
LIG-MnNiFe-1	0.569	1.543	~3.8-4.0	0.974
LIG-MnNiFe-2	0.586	1.566	~4.0	0.980

<sup>a</sup> ORR current density reaches -3 mA cm<sup>-2</sup>. <sup>b</sup> OER current density reaches 10 mA cm<sup>-</sup> <sup>2</sup>.

 Table 4.2. Summary of the ORR/OER performance of the LIG catalysts.

Catalyst	Preparation		OER Tafel slope	Dof
Catalyst	method <sup>a</sup>		(mV dec <sup>-1</sup> )	Kei
LIG-CoNiFe-1	LIG	1.517	41	
LIG-CoNiFe-2	LIG	1.529	38	This
LIG-MnNiFe-1	LIG	1.543	45	work
LIG-MnNiFe-2	LIG	1.566	47	
CoS <sub>x</sub> @PCN/rGO	ТР	1.57	44	186
Co-C <sub>3</sub> N <sub>4</sub> /CNT	ТР	1.61	68.4	187
NiCo/PFC	ТР	1.63	106	188
H-Pt/CaMnO <sub>3</sub>	ТР	1.80	-	189
Mn <sub>x</sub> O <sub>y</sub> /N-doped carbon	ТР	1.68	82.6	190
Co/Co3O4@PGS	ТР	1.58	76.1	191
S-GNS/NiCo2S4	ТР	1.56	65	192

<sup>a</sup> TP: thermal pyrolysis.

Table 4.3. Comparison of OER activities of the LIG-based catalysts with the state-of-the-art catalysts (in 0.1 M KOH).



#### Figure 4.12. Zn-air battery performance of the catalysts in aqueous electrolyte.

(a) Schematic structure of the battery. (b) Charge-discharge polarization curves of the batteries with different catalysts. (c) Discharge polarization curves and the corresponding power density. (d) Galvanostatic discharge-charge cycling curves of LIG-MnNiFe-1 and LIG-MnNiFe-2 at 10 mA cm<sup>-2</sup>. (e) Long time cycling test of LIG-MnNiFe-1 at 10 mA cm<sup>-2</sup> (arrows represent the supplement of electrolyte). (f) Photograph of two Zn-air batteries in serial connection, showing an open circuit potential of 2.84 V and (g) the LED (2.5 V) lighted by the batteries. (h) Photograph of the electric water splitting on catalytic LIG electrodes, LIG-Co-P and LIG-NiFe, powered by two Zn-air batteries in serial connection. Inset shows the zoomed photograph of the working electrodes.

With the dual ORR/OER electrochemical performances of the catalysts optimized, we then determined to incorporate them as the cathode catalyst in a home-made liquid Zn-air battery (**Figure 4.12a**). The battery charge/discharge performance was characterized by polarization curves as shown in **Figure 4.12b**. The incorporation of NiFe in the catalysts contributes to much lower charge voltages (LIG-CoNiFe-1, 2.09 V; LIG-CoNiFe-2, 2.13 V; LIG-MnNiFe-1, 2.11 V; LIG-MnNiFe-2, 2.25 V) than LIG-CoO<sub>x</sub> (2.26 V) at 50 mA cm<sup>-2</sup>. And the catalysts have shown performance comparable to Pt/C+RuO<sub>2</sub>. The LIG-MnNiFe-1 exhibits the lowest charge/discharge voltage gap of 1.09 V at 50 mA cm<sup>-2</sup>, which is even better than the performance of Pt/C+RuO<sub>2</sub> (1.22 V) or LIG-CoO<sub>x</sub> (1.31 V) (as measured by

us, not shown). The LIG-MnNiFe-1 delivered a maximum power density of 98.9 mW cm<sup>-2</sup>, followed by 95.1 mW cm<sup>-2</sup> from LIG-MnNiFe-2, both surpassing that of Pt/C+RuO<sub>2</sub> (93.8 mW cm<sup>-2</sup>). Although LIG-CoNiFe-1 and LIG-CoNiFe-2 have low overpotentials in the charge process, their output power densities were hindered by the ORR activity. Furthermore, at the discharge current density of 10 mA cm<sup>-2</sup>, the LIG-MnNiFe-1 battery exhibited a specific capacity of 807 mAh g<sub>Zn</sub>-1, corresponding to an energy density of 842 Wh kg<sub>Zn</sub>-1 (Figure 4.13). The rechargeability of the batteries with LIG-MnNiFe-1 and LIG-MnNiFe-2 catalysts was tested by galvanostatic charge/discharge (10 mA cm<sup>-2</sup>, 10 min/cycle) as shown in Figure **4.12**d, e and **Figure 4.14**. Both batteries showed excellent stability for >500 cycles. The round-trip voltage gap of LIG-MnNiFe-1 merely increased from 0.88 V in the initial cycles to 0.97 V after  $\sim$ 2000 cycles ( $\sim$ 350 h). And the voltage efficiency decreased only slightly from 57% to 53%. As for LIG-MnNiFe-2, the round-trip voltage gap increased from 0.89 V to 1.04 V after 500 cycles coupled with a decrease in efficiency from 57% to 51%. In contrast, the Pt/C+RuO<sub>2</sub> showed a higher roundtrip voltage gap of 0.96 V (Figure 4.15). The LIG method was further employed for the *in situ* preparation of the catalytic electrode MnNiFe/CFP (see experimental details), which could be directly used as the cathode in Zn-air battery. As shown in Figure 4.16, the MnNiFe/CFP exhibited good ORR/OER activity and the battery worked with good stability for over 1000 cycles under galvanostatic condition. The performance of the cathodes is strongly related to their element composition, as illustrated by their OER/ORR activities. Ni/Fe and Co species are highly active for

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OER but suffers from low electron transfer number in ORR, which results in the low power/energy densities. On the contrary, Mn species promote the overall ORR activity yet increase the OER overpotential, and the charging potential. Our results show that the ternary metal oxide strategy is an effective method for bifunctional catalyst design, while the elemental composition should be carefully selected to achieve an optimized energy efficiency in Zn-air batteries.



Figure 4.13. (a) Galvanostatic discharge profile of LIG-MnNiFe-1 at 10, 20, 40, 60, 80 and 100 mA cm<sup>-2</sup>. (b) Capacity and energy density of LIG-MnNiFe-1 as the cathode catalyst. Discharge curve of Zn-air batteries with LIG-MnNiFe-1 as the cathode catalyst under galvanostatic discharge until complete consumption of Zn.



Figure 4.14. Galvanostatic cycling performance of Zn-air battery with LIG-MnNiFe-2 as the cathode catalyst (10 mA cm<sup>-2</sup>, 10 min per cycle).



Figure 4.15. Galvanostatic discharge-charge curves of Pt/C+RuO<sub>2</sub>.



Figure 4.16. (a) OER/ORR polarization curve of MnNiFe/CFP. (b) Cycling performance of the MnNiFe/CFP cathode in a Zn-air battery.

As a demonstration for practical applications, two Zn-air batteries with LIG-MnNiFe-1 catalyst were serially connected to generate an output voltage of 2.84 V and power the LED (**Figure 4.12**f and g). Furthermore, the serial connected Zn-air batteries were employed to drive the electrical water splitting on catalytic LIG electrodes, LIG-Co-P and LIG-NiFe (**Figure 4.17**),<sup>193</sup> as shown in **Figure 4.9**h (**Video 4.1** and **Video 4.2**). The LIG derived materials exhibited great potential and applicability in electrochemical energy storage and conversion.



Figure 4.17. Polarization curves of (a) LIG-Co-P and (b) LIG-NiFe electrodes in 1 M KOH.



Figure 4.18. Cycling performance of the flexible Zn-air battery.

**Table 4.4** summarizes the performance of rechargeable Zn-air batteries with
 various bifunctional electrocatalysts. The ternary metal oxide/LIG catalysts exhibited comparable performance in terms of power and energy density to those conventionally prepared catalysts. And the battery with our catalysts has shown remarkably high durability, which is attributed to the high OER activity of the catalysts. In a Zn-air battery, the charging process is essentially the plating of Zn at the anode, coupled with the OER at the cathode. The OER generally shows high overpotential and Tafel slopes, which results in a high charging voltage of the battery as well as a high anodic condition on the cathode (even the current collector). The latter would easily cause the corrosion of the air cathode that leads to leakage/flooding of the electrolyte and the oxidation of ORR sites,<sup>160, 194</sup> both hampering the durability of the battery. In view of these problems, the hybrid metal oxides provide OER and ORR sites from different metal species in the nanoparticles, to prevent the deactivation of the ORR site under anodic condition. Instead of using a 3-electrode configuration,<sup>194</sup> our strategy provides the facile synthesized ternary metal oxide/graphene catalysts with high bifunctional activity, specifically the OER performance, to minimize the overpotential in the charging process and to enhance the durability of the batteries.

Catalyst	Energy density (Wh kg <sub>Zn</sub> -1)	Max power (mW cm <sup>-2</sup> )	Voltage gap (V)ª	Cycling stability	Ref	
LIG-MnNiFe-1	842	98.9	0.88 (10)	$10 \text{ mA cm}^2$ $10 \text{ min}/\text{cycle} > 500 \text{cycles}$		
LIG-MnNiFe-2	-	95.1	0.89 (10)	10 IIIA cili 2, 10 IIIII/ cycle, >500 cycles		
NGM-Co	840	152	1.0 (2)	2 mA cm <sup>-2</sup> , 20 min/cycle for 180	195	
				cycles		
$Co_3O_4$	_	40	1 16 (50)	50 mA cm <sup>-2</sup> , 10 min/cycle for 100	196	
nanowires/SS		40 1.10 (30)	cycles			
Ag-Cu on Ni foam			0.96 (20)	20 mA cm <sup>-2</sup> , 20 min/cycle for 100		
	641	86		cycles	197	
NCNT/CoO-				20 mA cm <sup>-2</sup> , 10 min/cycle for 100		
NiONiCo	713	102	0.86 (20)	cycles	198	
Co/Co <sub>3</sub> O <sub>4</sub> @PGS	-	118	0.91 (10)	10 mA cm <sup>-2</sup> , 10 min/cycle for 800h	191	
Co(OH)2+N-rGO			1.29 (15)	15 mA cm <sup>-2</sup> , 40 min/cycle for 75		
	-	36		cycles	154	
Co-N,B-CSs	-	100.4	1.35 (5)	5 mA cm <sup>-2</sup> , for 128 cycles	199	
NCNT/Co <sub>x</sub> Mn <sub>1-x</sub> O	695	81	0.57 (7)	7 mA cm <sup>-2</sup> , 10 min/cycle for 70 cycles	200	
N-doped graphene			0.86~1.06	2 mA cm <sup>-2</sup> , 60 min/cycle for 160		
nanoribbon	-	65	(2)	cycles	172	

<sup>a</sup>Current density shown in parenthesis, unit is mA cm<sup>-2</sup>.

Table 4.4 The performance of rechargeable Zn-air batteries with variousbifunctional electrocatalysts.



Figure 4.19. Flexible Zn-air battery with LIG-MnNiFe-1 as the cathode catalyst.

(a) Schematic structure of the flexible Zn-air battery. (b) Charge-discharge polarization curves of the battery. Inset shows the open-circuit potential. (c) Photograph showing the open-circuit potential of the battery. Inset shows the side-view photograph. (d) Photograph of a LED driven by the serial connection of two flexible batteries.

Inspired by the performance of LIG-MnNiFe-1, we fabricated a flexible Zn-air battery with LIG-MnNiFe-1 supported on carbon cloth as the air cathode and Zn plate as the anode as illustrated in **Figure 4.19**a.<sup>201</sup> The battery exhibited a high open-circuit potential of 1.35 V and a good rechargeability as shown in **Figure** 

**4.19**b and c. For a practical demonstration, the serial connected devices were capable of powering a LED. The long-term cycling performance is characterized in **Figure 4.18**, which indicates the good durability of the flexible battery. In contrast to the traditional Zn-air batteries with liquid electrolyte, the flexible batteries show more attractive characters including flexibility, small size, safety and variability.

### 4.2.3. Conclusion

In summary, a series of bifunctional hybrid catalysts were prepared through a facile LIG process. The ternary metal oxide/LIG hybrid catalysts were directly formed by re-lasing on precursor-loaded LIG using a  $CO_2$  laser. All the catalysts have shown good ORR/OER bifunctionality and demonstrate promising applications and they were optimized to afford excellent cathode catalysts for rechargeable Zn-air batteries. The optimum activity of LIG-MnNiFe-1 outperformed the noble metal Pt/C + RuO<sub>2</sub> benchmark in terms of lower charge/discharge overpotential, higher output power and more favorable reaction kinetics. The improved OER activity of the catalysts significantly lowers the overpotential in the charging process, which helps to avoid the oxidation of the ORR active sites under anodic conditions. The batteries have shown considerably high stability for >500 cycles with small increases in the charge/discharge voltage gap over 350 h. There could be several reasons for the superior performance of LIG-MnNiFe-1: (a) there is a porous and interconnected carbon structure to anchor the nanoparticles that enables high active surface area with good electrical conductivity; (b) there is an optimized ratio of metal species in the nanoparticles resulting in a balanced OER/ORR activity; (c) there are separate

OER and ORR sites designed to enhance the durability of the catalyst. The catalysts also demonstrate their potential for applications in flexible Zn-air batteries for wearable and flexible electronic devices. Furthermore, the study presented here can lead to a better route to develop high-performance non-precious metal bifunctional catalysts for metal-air batteries through a scalable and cost-effective LIG approach.

# Video 4.1. real-time videos of the water splitting powered by all-LIG materials (top view)

https://pubs.acs.org/doi/abs/10.1021/acsaem.8b02011

Video 4.2. real-time videos of the water splitting powered by all-LIG materials (side view)

https://pubs.acs.org/doi/abs/10.1021/acsaem.8b02011

### 4.3. Experimental Contributions

**Muqing Ren** designed the experiments, prepared the samples, and conducted part of the characterizations including SEM, TEM, Raman, XPS, electrochemical measurements, battery test. Jibo Zhang designed part of the experiments and conducted part of the characterizations including, electrochemical measurements, SEM and XRD.

# Chapter 5

### Li-breathing Air Batteries Catalyzed by MnNiFe/Laser-Induced Graphene Catalysts

This chapter was entirely copied from reference 202.

### **5.1. Introduction**

The ever-increasing demand on energy storage for many applications including electrical vehicles, portable electronic devices and grid electricity storage, has stimulated significant advances in rechargeable batteries. Secondary Li-ion batteries have shown remarkable success in the past decades; however, their energy densities are insufficient to meet the demands for future applications.<sup>203, 204</sup> Rechargeable metal-O<sub>2</sub> (or air) batteries are receiving much interest due to their high specific energy exceeding that of conventional Li-ion batteries, and they are therefore being considered the next generation device for high energy density and energy storage needs.<sup>205, 206</sup> Among the metal-air batteries, Li-air and Na-air are the most attractive due to their high theoretical energy densities of 3456 Wh/kgLi202 and 1105 Wh/kg<sub>Na02</sub>, respectively, both being much higher than that of the Li-ion batteries (~400-500 Wh/kg).<sup>204, 207, 208</sup> Generally, the operation of rechargeable metal- $O_2$  batteries is enabled by the reversible formation/decomposition of discharge product (usually the metal oxide or peroxide) at the cathode coupled with the stripping/plating process of metal at the anode. One of the key challenges of the realization of metal-O<sub>2</sub> batteries is the high overpotentials and sluggish kinetics of the oxygen electrochemistry at the cathode, the oxygen reduction (discharge) and evolution (charge) processes.<sup>209-211</sup> Therefore, many issues remain to be overcome, such as the low electrical conductivity of the discharge products, aggregation of discharge products on the air cathode, intrinsic sluggish oxygen kinetics at the cathode, and the poor electrode-electrolyte interface.<sup>212-214</sup>

The implementation of carbon-composite catalysts on the cathode has been regarded as an effective method to solve the above issues. Benefiting from the high surface area and electrical conductivity of the carbon matrix, the bifunctional oxygen electrocatalysts can remarkably lower the overpotential for oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) and extend the cycle life of metal-O<sub>2</sub> batteries.<sup>180, 215, 216</sup> While noble metal catalysts (Au, Pt, RuO<sub>2</sub> and IrO<sub>2</sub>) have demonstrated their superior electrocatalytic performance,<sup>80, 217-220</sup>

they are limited due to their high cost and scarcity. Alternatively, non-noble metal catalysts have been developed as cost-effective alternative for metal-O<sub>2</sub> batteries. For instance, the newly developed Fe/N/C composites could reduce both the discharge and charge overpotentials when used as the cathode catalyst in Li-O<sub>2</sub> batteries.<sup>221</sup> NiMn<sub>2</sub>O<sub>4</sub> showed enhanced performance towards ORR and OER reactions in Li-O<sub>2</sub> batteries when compared to pristine carbon particles.<sup>222</sup> The carbon dots-decorated CoO/C composites with oxygen vacancies enhanced the Li-O<sub>2</sub> battery cycling stability by 2X when compared to the conventional CoO catalysts.<sup>223</sup> However, most of these bifunctional catalysts for metal-air batteries are tested in pure O<sub>2</sub> atmosphere, but a testing atmosphere imitating ambient conditions is desired. Moreover, the Li-air battery in atmospheric conditions has discharge products such as LiOH, Li<sub>2</sub>CO<sub>3</sub>, and Li<sub>2</sub>O<sub>2</sub>, whereas the decomposition potential of LiOH and Li<sub>2</sub>CO<sub>3</sub> is above 4.3-4.6 V (*vs* Li<sup>+</sup>/Li),<sup>224</sup> much higher than that of Li<sub>2</sub>O<sub>2</sub> (2.97 V) which is preferentially formed in pure O<sub>2</sub>. Hence, a study on the battery

Our group has recently developed a series of methods to prepare metal oxide/laser-induced graphene (LIG) composites through facile procedures that are oven-free.<sup>70, 114</sup> LIG is a 3D porous graphene formed by a one-step laser scribing process on commercial polyimide (PI, Kapton®) film.<sup>1</sup> A typical CO<sub>2</sub> laser cutter as found in most machine shops can be used for this work. The process is scalable and amendable to roll-to-roll processing on plastic films. Further, it is simple to have enhanced activity through nanoparticle incorporation during the lasing process.

performance in an air environment is necessary.

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LIG-derived catalysts benefit from high electrical conductivity and porosity. The catalysts have exhibited high activities for electrocatalytic processes in aqueous electrolytes for water splitting, oxygen reduction/evolution and Zn-air batteries.<sup>158</sup> In view of the high ORR/OER activity of the transition metal oxides of the fourth period in aprotic electrolyte,<sup>225</sup> we present the ternary metal oxides/LIG composites as cathode catalysts for both Li-O<sub>2</sub> batteries in pure O<sub>2</sub> and Li-air batteries tested in breathing air atmosphere. The specific selection of ternary system with Mn, Ni, Fe was based on our previous studies on the OER and ORR activities in aqueous electrolytes<sup>[40]</sup> that demonstrated that Mn, Ni, Fe ternary oxides exhibited overall excellent OER/ORR bifunctionality in aqueous electrolyte (O2 electrocatalysis and Zn-air battery). The Mn, Ni, Fe ternary oxides showed lower overpotential for OER, ORR and excellent electron transfer number, demonstrating better performance than Co, Ni, Fe ternary oxides. Generally, a high activity in aqueous electrolyte can imply a good activity in aprotic electrolyte.<sup>208</sup> The preliminary results inspired us to further study the performance of Mn, Ni, Fe-derived ternary oxides in aprotic Li-O<sub>2</sub> batteries. For example, our previously investigated LIG-derived metal oxides have shown remarkably low overpotentials in  $O_2$  electrochemistry and an excellent electron transfer number of 4 in aqueous electrolyte, leading to a high energy density rechargeable Zn-air battery. MnNiFe/LIG composites with different element compositions were synthesized and denoted as M111/LIG (Mn: Ni: Fe = 1:1:1) and M311/LIG (Mn: Ni: Fe = 3:1:1), respectively. Both M111/LIG and M311/LIG catalysts have demonstrated superior stability and enhanced cycling life in the Li-air

batteries without the presence of a redox mediator such as LiI, LiBr, tetrathiafulvalene (TTF) and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO).<sup>226-229</sup> The Li-O<sub>2</sub> battery with M311/LIG catalyst can be reliably discharged and charged for 150 cycles with the discharge potential slightly increasing by 0.24 V. The Libreathing air battery with M311/LIG catalyst can be cycled for 350 cycles while Libreathing air with M111/LIG catalysts can cycled for ~ 300 stable cycles. The morphology and structure of products during battery cycling were also investigated to better understand the fundamental electrocatalytic mechanisms.

### 5.2. Li-breathing Air Batteries Catalyzed by MnNiFe/Laser-Induced Graphene Catalysts

#### 5.2.1. Experimental Section

#### 5.2.1.1. Material Synthesis

*Preparation of the catalyst:* All samples were prepared under ambient air. Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser (10.6 μm, Universal XLS10MWH laser cutter platform) on the PI film in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2×2 cm<sup>2</sup> square. All of the catalysts were prepared as previously discussed. 1 M MnSO<sub>4</sub>, 1 M Ni(NO<sub>3</sub>)<sub>2</sub> and 1 M Fe(NO<sub>3</sub>)<sub>3</sub> solutions were prepared with deionized water. Then the solutions with different molar ratios were prepared with the total concentration of metal cations kept at 1 M. The as-prepared LIG ( $2 \times 2 \text{ cm}^2$ ) was treated by O<sub>2</sub> plasma (Model 1020 Plasma Cleaner, Fischione Instruments) for 5 min to increase the wettability with the precursor solutions. 80 µL of the metal cation solutions were dropped uniformly onto the LIG. The soaked LIG (on PI) was dried under vacuum (~120 mm Hg) for 6 h. The LIG was lased again atop the previous LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). The powder was scratched off the PI using a spatula and collected for characterization.

#### 5.2.1.2. Materials characterization

*Materials characterization*: SEM images were obtained by a FEI Quanta 400 highresolution field emission SEM. TEM images measurements were carried out at 80 keV using a FEI Titan Themis3 S/TEM equipped with image and probe spherical aberration correctors. XPS was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al K $\alpha$  X-ray line source, 45° take off angle, and a 200 µm beam size. Raman spectroscopy was performed at 532 nm laser excitation. XRD measurement were done by a Rigaku SmartLab Intelligent X-ray diffraction system with filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å). A piece of Kapton® thin film covered the sample to minimize the exposure to moisture.

*Battery test*: The electrochemical performance of M111/LIG and M311/LIG bifunctional catalysts was tested in Li-O<sub>2</sub>, Li-air and Na-air cells through coin type CR2032 cells. All of the cells were assembled in the glove box under argon atmosphere. The CR2032 Li-O<sub>2</sub> and Li-air cell includes the lithium foil, Celgard 2500 membrane, 1 M lithium bistrifluoromethanesulfonimidate /tetraglyme (LiTFSI/G4)

and the air cathode electrode. The CR2032 Na-air cell includes the sodium foil, Celgard 2500 membrane, 1 M sodium perchlorate /tetraglyme (NaClO<sub>4</sub>/G4) and the air cathode electrode. The cathode was prepared by casting slurry which consists of 80 wt% catalysts, 10 wt% carbon black (Super P, TIMCAL) and 10 wt% polyvinylidene difluoride (PVDF; Alfa Aesar) in *N*-methyl-2-pyrrolidone (NMP) on a piece of carbon paper. The galvanostatic discharge/charge tests were carried out in voltage range of 2.0 to 4.5 V (vs Li/Li<sup>+</sup>). The input O<sub>2</sub>/air was filter through Ascarite/desiccant to remove the moisture and CO<sub>2</sub>.

#### 5.2.2. Result and Discussion

M111/LIG and M311/LIG catalysts were synthesized in a solid phase process similar to the previously developed methods.<sup>158</sup> Briefly, LIG was first obtained through lasing of a PI sheet followed by the O<sub>2</sub>-plasma treatment to enhance the hydrophilicity. Then the aqueous precursor solutions, 1 M MnSO<sub>4</sub>, 1 M Ni(NO<sub>3</sub>)<sub>2</sub> and 1 M Fe(NO<sub>3</sub>)<sub>3</sub> with desired molar ratio (1:1:1 and 3:1:1) are dripped onto the LIG pattern using a pipet. The porous LIG with enhanced wettability uniformly adsorbs the solutions and therefore the metal salts are well-distributed in the LIG after a drying process. Subsequently, a second laser scribing was carried out atop the original LIG. This converts metal salts to metal oxides that are graphene-surrounded. Then the resultant powders are collected and applied as the catalysts for the batteries.

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Figure 5.1. TEM images of (a) M111/LIG and (b) M311/LIG catalysts.


Figure 5.2. Electrochemical performance of the Li-O<sub>2</sub> batteries.

Galvanostatic cycling performance of (a) M111/LIG and (b) M311/LIG catalysts for Li-O<sub>2</sub> batteries. Full discharge and charge capacity of (c) M111/LIG and (d) M311/LIG catalysts for Li-O<sub>2</sub> batteries.

The characteristic morphology of the catalysts is shown by the TEM images in **Figure 5.1**. Both catalysts demonstrate the nanoparticles that are embedded on graphene. The M311/LIG mainly consists of nanoparticles that are uniformly distributed on LIG graphene foam with a comparatively smaller diameter of  $\sim 5$  nm than that in M111/LIG. The TEM images shows that both M311/LIG and M111/LIG have a quite uniform spatial distribution on the graphene structures. The main difference is the size distribution of the particles. M311/LIG exhibits, on the average, smaller nanoparticles than M111/LIG. The LIG process undergoes rapid heating and cooling, and the transient local temperature can reach >2000 K. Noting that Ni and Fe species are good catalysts for carbon growth, they exhibit good solubility for carbon at high temperature. The higher atomic ratio of Ni/Fe (~67% vs 40% in M311/LIG) in the synthesis of M111/LIG can lead to the aggregation of metal species, and their properties in dissolving carbon could also facilitate the process. Additionally, under the extremely high temperature, part of the metal species can be reduced by carbon to elemental metal. Both Ni and Fe have higher thermal stability than Mn, and might initiate the nucleation process. Thus, in the M111/LIG, the initial nucleation of Ni/Fe may be the dominant process when compared to Mn, and could lead to a different size distribution of the nanoparticles. The difference in particle

size indicates a higher surface-area-to-volume ratio of M311/LIG, and thus more exposed active sites than in M111/LIG. It should be noted that the ternary nature of the nanoparticles was confirmed by elemental mapping,<sup>158</sup> and therefore a synergetic effect between the species is also expected.



Figure 5.3. Discharge and charge mid-voltage *vs* the cycle number of Li-O<sub>2</sub> batteries with (a) M111/LIG and (b) M311/LIG as the cathode catalyst.

**Figure 5.2**a and b show the representative discharge and charge voltage profiles for the M111/LIG and M311/LIG catalysts at a current density of 0.08 mA/cm<sup>2</sup> with a cutoff capacity of 0.4 mAh/cm<sup>2</sup>. The charge mid-voltage of the fifth cycle in the M111/LIG in the Li-O<sub>2</sub> battery is remarkably lower (0.09 V) than in M311/LIG, however, the charge mid-voltage value for the Li-O<sub>2</sub> (M111/LIG) battery kept increasing with the increase in cycle numbers while the mid-voltage values of Li-O<sub>2</sub> (M311/LIG) was much more stable and the charging voltage slightly increased by 0.31 V (**Figure 5.3**). It should be noted that the intrinsic activity of LIG and the gas diffusion layer (carbon fiber paper) have been investigated, both exhibiting poor

cycling stability with high overpotentials.<sup>1, 114</sup> The results suggest that higher Mn content leads to a better ORR/OER activity. The tetraglyme-based Li<sup>+</sup> electrolyte, the preferential discharge/reduction product of O<sub>2</sub> is Li<sub>2</sub>O<sub>2</sub>, is poorly conductive.<sup>230, 231</sup> As the cycle numbers increased, the insulating discharge products (that are not fully decomposed during the charge process) can build on the surfaces of the catalysts. Such aggregation will not only increase the internal resistance but also block the O<sub>2</sub> diffusion to the catalyst, leading to a gradually increasing overpotential in both discharge and charge processes. The deep-voltage cycling performance provides support for this hypothesis. As shown in **Figure 5.2**c and d, the discharge capacity of the Li-O<sub>2</sub> battery with the M311/LIG catalyst (vs Li<sup>+</sup>/Li) reached 26.3 mAh/cm<sup>2</sup> at 2.0 V, which nearly doubled that of the M111/LIG catalyst (11.9 mAh/cm<sup>2</sup>). The higher capacity suggests there are more accessible ORR active sites in M311/LIG than in M111/LIG, which is in accord with the observations in the TEM. Although both M111/LIG and M311/LIG exhibit good rechargeability, the successive accumulation of small amounts of undecomposed discharge products will become significant upon long-term cycling. Since the electrochemical reactions at the cathode are heterogeneous, the aggregation of insulating species on the surface of the catalysts may diminish their intrinsic high activity. The enhanced cycling performance of M311/LIG catalyst (Figure 5.3) not only demonstrates its high catalytic activity but may imply an improved surface morphology of the discharge product on the catalyst.

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Figure 5.4. Electrochemical performance of the Li-air batteries with M111/LIG catalyst.

(a) Galvanostatic cycling performance and (b) the discharge and charge midvoltage *vs* cycle number.



Figure 5.5. Electrochemical performance of the Li-air batteries with M311/LIG catalyst.

### (a) Galvanostatic cycling performance and (b) the discharge and charge midvoltage vs cycle number.

Instead of using pure oxygen, M111/LIG and M311/LIG catalysts were tested in filtered breathing air (see experimental section). M111/LIG enables the Li-air battery to reliably discharge and charge for 300 cycles with a cut-off capacity of 0.4 mAh/cm<sup>2</sup>. The charge overpotential increased by 0.94 V after 300 cycles (Figure 5.4). The M311/LIG catalyst could produce a 350 cycle Li-air battery with the charge overpotential increase of 0.57 V (Figure 5.5). The slightly higher cyclability in air than in  $O_2$  might originate from the less passivated Li anode due to the lower partial pressure in air. The O<sub>2</sub> crossover towards anode can lead to the formation of insulating products that increase the overpotential of Li platting/stripping.<sup>232-234</sup> Apart from the anode side, the cathodic results suggest that although Ni-Fe species are OER-active catalysts and present in both M111/LIG and M311/LIG, the higher Mn content in the catalyst leads to a higher evolution of O<sub>2</sub> during the charge process. Indeed, Mn-based catalysts have been reported to be efficient in OER.<sup>75, 235-</sup> <sup>237</sup> M111/LIG and M311/LIG were compared with other reported ternary metal oxides for Li-O<sub>2</sub> batteries (**Table 5.1**); both catalysts show an enhanced stability and cycle life.

Catalyst	Electrolyte	Cycle	Battery type	Ref
α-MnO2@GN	0.5 M LiClO <sub>4</sub> /DMSO	45 (1000	Li-O <sub>2</sub> (Swagelok	238

composite		mAh/g)	cell)	
Carbon nanosheets/moly bdenum carbide	1 M LiTFSI/TEGDME	70 (1000 mAh/g)	Li-O <sub>2</sub> (2032 coin- cells)	239
PdNi-NSMmC/CP	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	74 (500 mAh/g)	Li-O2 (Swagelok cell)	240
CoO/rGO	1 M LiTFSI/TEGDME	69 (1000 mAh/g)	Li-O2 (Swagelok cell)	241
Pt-Cu/C	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	50 (500 mAh/g)	Li-O2 (Swagelok cell)	242
C-C03O4-IO	1 M LiTFSI/TEGDME	20 (500 mAh/g)	Li-O2 (Swagelok cell)	69
C <sub>x</sub> N <sub>y</sub> particles@N- doped porous graphene	1 M LiTFSI/TEGDME	200 (1000 mAh/g)	Li-O <sub>2</sub> (2032 coin- cells)	243
N-Doping Cobalt@Graphene	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	30 (1 mAh/cm²)	Li-O2 (Swagelok cell)	244
Co[Co, Fe]O <sub>4</sub> /NG	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	110 (1000 mAh/g)	Li-O <sub>2</sub> (2032 coin- cells)	245
Co-Mn-O MOFs	1 M LiCF <sub>3</sub> SO <sub>3</sub> /TEGDME	100 (0.16 mAh/cm <sup>2</sup> )	Li-O2 (2032 coin- cells)	246
CoFe <sub>2</sub> O <sub>4</sub> /CNT	1 M LiTFSI/TEGDME	30 (430 mAh/g)	Li-O2 (Swagelok cell)	247
CoFe <sub>2</sub> O <sub>4</sub>	1 M LiTFSI/TEGDME	47(500 mAh/g)	Li-O2 (Swagelok cell)	248
M111/LIG	1 M LiTFSI/TEGDME	150 (0.4 mAh/cm <sup>2</sup> ) ca. 430 mAh/g <sub>catalyst</sub>	Li-O2 (2032 coin- cells)	This work
M111/LIG	1 M LiTFSI/TEGDME	300 (0.4 mAh/cm <sup>2</sup> ) ca. 430 mAh/g <sub>catalyst</sub>	Li-air (2032 coin- cells)	This work
M311/LIG	1 M LiTFSI/TEGDME	150 (0.4 mAh/cm <sup>2</sup> ) ca. 430 mAh/g <sub>catalyst</sub>	Li-O <sub>2</sub> (2032 coin- cells)	This work
M311/LIG	1 M LiTFSI/TEGDME	350 (0.4 mAh/cm <sup>2</sup> ) ca. 430 mAh/g <sub>catalyst</sub>	Li-air (2032 coin- cells)	This work

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Table 5.1. Comparison of the M111/LIG and M311 catalysts with metal oxides/graphene catalysts.

For a fundamental understanding on the mechanism of the M111/LIG and M311/LIG catalysts in the batteries, O<sub>2</sub> was preferred since the electrochemistry in breathing air will be more complicated due to the side reactions and products. For example, Li can react with N<sub>2</sub> to form Li<sub>3</sub>N. Li<sub>3</sub>N is considered a good SEI layer promoter for protecting Li metal anode<sup>249-251</sup>, therefore, it will influence the cycling performance of the battery.



Figure 5.6. Catalyst morphology, as shown by SEM,

## of (a) the pristine M111/LIG electrode, (b) the discharged M111/LIG electrode, (c) the charged M111/LIG electrode, (d) the pristine M311/LIG electrode, (e) the discharged M311/LIG electrode and (f) the charged M311/LIG electrode.

**Figure 5.6** summarizes the morphological changes of the catalysts after a deep discharge-charge cycle as shown by scanning electron microscopy (SEM). The typical morphologies of pristine M111/LIG and M311/LIG electrode are shown in **Figure 5.6**a and d, exhibiting a highly porous structure in the LIG-derived catalysts.<sup>1, 70, 114, 158</sup> These porous structures facilitate the fast diffusion of O<sub>2</sub>, and also provide a conductive and high surface area host that interacts with the electrolyte to maximize the accommodation of discharged products. After a deep discharge to 2.0 V in  $O_2$  atmosphere, both M111/LIG and M311/LIG were covered by particles of the discharge product as shown in **Figure 5.6**b and e. Interestingly, the discharge products on M111/LIG are aggregates of particles with diameters < 1μm. In contrast, the discharge products on M311/LIG are well-dispersed smooth particles with a larger diameter of  $\sim$ 1-2 µm. Despite the difference in particle size, both discharge products possess morphologies similar to crystalline Li<sub>2</sub>O<sub>2</sub>.<sup>252</sup> However, the significant variance in the size and configuration of particles might imply a fundamentally different nucleation processes in each catalyst. After the electrodes were fully charged, the particles disappeared, and the morphology resembled the pristine catalysts as shown in Figure 5.6c and f, suggesting the decomposition of discharge products. Although the results indicate a similar activity for M111/LIG and M311/LIG catalysts in the reversible formation and

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decomposition of discharge products in a Li-O<sub>2</sub> battery, a further detailed investigation was conducted.



Figure 5.7. XRD characterizations of the (a) M111/LIG and (b) M311/LIG electrodes.

The crystalline structure changes of the discharge products during discharge and charge process in a Li-O<sub>2</sub> battery were obtained from the X-ray diffraction (XRD) data (**Figure 5.7** a and b). In addition to the characteristic peak of multilayer graphene observed at 25.6°, two major products are identified after the discharge process: LiOH and Li<sub>2</sub>O<sub>2</sub>. At room temperature, Li<sub>2</sub>O<sub>2</sub> is both the thermodynamically and kinetically stable product of oxygen reduction in aprotic Li<sup>+</sup> electrolytes, due to the higher change in Gibbs free energy ( $\Delta$ Gr<sup>0</sup>(Li<sub>2</sub>O<sub>2</sub>) = -571 kJ/mol,  $\Delta$ Gr<sup>0</sup>(Li<sub>2</sub>O) = -561 kJ/mol) and the high activation energy required to break the O-O bond.<sup>253</sup> In a typical ORR process, O<sub>2</sub> is reduced to O<sub>2</sub><sup>--</sup> which precipitates with Li<sup>+</sup> to form LiO<sub>2</sub> in low donor number solvent, such as the ethers used in this study.<sup>[3]</sup> The subsequent reduction from LiO<sub>2</sub> to Li<sub>2</sub>O<sub>2</sub> is accomplished through the reduction and/or disproportionation of LiO<sub>2</sub> deposited on the cathode surface, which highlights the surface catalytic activity of the O<sub>2</sub> electrode.

The formation of LiOH in the Li-O<sub>2</sub> battery could be ascribed to several processes. The reaction between  $Li_2O_2$  and trace amounts of  $H_2O$  in the electrolyte/O<sub>2</sub> atmosphere leads to the formation of LiOH ( $2Li_2O_2 + 2H_2O \rightarrow 4LiOH + O_2$ ). Another plausible source for LiOH is the high reactivity of LiO<sub>2</sub> with the PVDF binder as shown in **Equation 5.1**: <sup>254-256</sup>

$$\text{LiO}_2 + -(\text{CH}_2\text{-}\text{CF}_2) - \rightarrow \text{HO}_2 + -(\text{CH}=\text{CF}) - + \text{LiF}$$

$$2\mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$$

### **Equation 5.1. Plausible source for LiOH.**

Mn species would facilitate the decomposition of H<sub>2</sub>O<sub>2</sub> and move the reaction forward to result in the formation of LiOH.<sup>255</sup> This process is also suggested by the slightly higher intensity of LiOH in the M311/LIG catalyst. Since the characteristic layering morphology of LiOH is not observed in the SEM images, we conclude that the formation of LiOH is not the major process in the batteries and would precipitate as small particles along with Li<sub>2</sub>O<sub>2</sub> formation.<sup>254</sup> Despite the dual discharge products, both catalysts have shown remarkably high activity in decomposing the discharge products during the charge process, as indicated by the loss of crystalline structures from the charged electrodes. The higher oxygen

evolution activity of NiFe species over Mn species would contribute to a lower overpotential of M111/LIG than in M311/LIG.<sup>257</sup> <sup>258</sup> As shown in **Figure 5.3**, M111/LIG exhibits a comparatively lower charge voltage than in M311/LIG in the first few cycles. However, as the cycling continued, the high activity NiFe species would be compensated by the increase of electrode polarization caused by irregular accumulation of discharge products, resulting in a higher overpotential. As shown in **Figure 5.2**, M111/LIG showed a charge voltage of ~3.82 V at the 5<sup>th</sup> cycle, which is lower than that of M311/LIG (~3.97 V). However, at the 25<sup>th</sup> cycle, the voltage of M111/LIG is 60 mV higher than that of M311/LIG (4.07 V vs 4.01 V). During the discharge/charge cycles, the peaks from the discharge products were barely observed, possibly due to the strong signals from the LIG. The graphenic structure of LIG is maintained as suggested by the Raman spectra (**Figure 5.8**), which suggests the excellent structural stability of the LIG catalysts even under high anodic conditions.



Figure 5.8. Raman spectra of the M111/LIG and M311/LIG electrodes.



Figure 5.9. High-resolution XPS characterization of (a, b) Li 1s and (c, d) O1s regions of the catalysts.

The chemical composition of the discharged and charged electrodes were studied by X-ray photoelectron spectroscopy (XPS) (**Figure 5.9**). The elemental compositions of the pristine catalysts have been well studied.<sup>202</sup> Among the catalysts, Ni and Fe species are in +2 (Ni  $2p_{3/2}$  856.1 eV) and +3 (Fe  $2p_{3/2}$  711.1 eV)

states, respectively. The Co species exhibits a combination of +3 (780.6 eV) and +2(782.7 eV) oxidation states. The +4 oxidation state of Mn was confirmed by the spinorbit splitting of 11.7 eV between Mn 2p<sub>2/3</sub> (641.8 eV) and 2p<sub>1/2</sub> (653.5 eV).<sup>202</sup> After discharging the electrode, Li 1s peaks emerged at  $\sim$ 55 eV (Figure 5a and 5b), which could be deconvoluted to Li<sub>2</sub>O (53.6 eV) and LiOH/Li<sub>2</sub>O<sub>2</sub> (54.5 eV). Simultaneously, The main peak of O1s for both discharged M111/LIG and M311/LIG electrodes (Figure 5.9 c), located at ~ 530.9 eV, demonstrates the presence of  $Li_2O_2/LiOH$ , since the Li 1s binding energies of  $Li_2O_2$  and LiOH overlap. The binding energy of Li 1s at 53.6 eV is ascribed to Li<sub>2</sub>O, which is in accordance with previous observations.<sup>253, 259</sup> The presence of Li<sub>2</sub>O is possibly due to the exposure to ambient air during the transfer of samples, because of the absence of Li<sub>2</sub>O features in the XRD results.<sup>260</sup> Both O 1s and Li 1s spectra of the electrodes have demonstrated the activity of the catalysts in the formation and decomposition of the discharge products: Li<sub>2</sub>O<sub>2</sub>/LiOH. In the Li 1s spectra, the predominant peak at 54.5 eV diminished when the electrode was charged, which accords well with the decrease of the O 1s peak at 530.9 eV.



Figure 5.10. The schematic discharge process of (a) M111/LIG and (b) M311/LIG. (c) CV curves of the Li-O<sub>2</sub> battery with different catalyst electrodes in O<sub>2</sub> atmosphere. (d) EIS analysis of the Li-O<sub>2</sub> batteries at different cycles (recorded at charged state).

The results from SEM, XRD and XPS suggest that the key factors to increase the performance of a Li-O<sub>2</sub> battery is not only to promote the catalytic activity of the O<sub>2</sub> electrode, but also to tailor the accumulation morphology of discharge products to facilitate the charge transfer and ion diffusion. As proposed in **Figure 5.10**, the

particles in M311/LIG have a higher density of surface active sites on the electrode due to the smaller particle size than in M111/LIG (Figure 5.1), as well as a higher content of Mn species that are active towards oxygen reduction. During the discharge process,  $O_2$  would first undergo a one-electron reduction to  $O_2$ .<sup>--</sup> and precipitate with Li<sup>+</sup> as LiO<sub>2</sub> because of the low donor number of the ether electrolyte (tetraglyme).<sup>205</sup> The reaction of LiO<sub>2</sub> leads to the discharge products. At the initial stage, the discharge products preferentially deposit on the catalyst particles due to their high affinity for oxygen. As the discharge continues, the exposed catalyst particles would be gradually covered by the discharge products. For the M111/LIG, which has fewer surface active sites, discharge products would completely cover the sites and start to precipitate irregularly on the electrode surface, eventually blocking the  $ion/O_2$  diffusion and reaching maximum capacity. The irregular precipitation is suggested to be a heterogeneous nucleation and results in the accumulation of small particles as shown in Figure 5.5b. Since M311/LIG has a much higher density of active sites, the discharge products could be favorably hosted on the catalyst surface as small particles even as the discharge capacity increases. This process might be a surface-assisted homogeneous nucleation process. The surface active sites would further lead to the growth of large particles as shown in **Figure 5.5**e, and a higher discharge capacity than in M111/LIG. During the charge process, the discharge products that are deposited far from the catalyst particles (as those on M111/LIG) might require a high overpotential to decompose,

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thus leading to an incomplete decomposition. The accumulation of poorly

conductive discharge products on the cathode results in high internal resistance and/or poor ion/ $O_2$  diffusion that causes the battery to fail.



Figure 5.11. Equivalent circuit for the fitting of EIS data.

 $R_{\rm s}$  stands for the equivalent serial resistance.  $C_{dl}$  anode and  $C_{dl}$  cathode stand for the double-layer capacitance at the anode and cathode, respectively.  $R_{CT}$  anode and  $R_{CT}$  cathode stand for the charge-transfer resistance at the anode and cathode, respectively.  $W_{\rm s}$  is the Warburg impedance.

In order to support this hypothesis, we recorded the cyclovoltammetry (CV) results of the catalysts as illustrated in **Figure 5.10c**. In an O<sub>2</sub> atmosphere, both catalysts showed the electrochemical signals towards the formation and decomposition of discharge products. M111/LIG and M311/LIG exhibited similar onset potential of oxygen reduction at ~2.8 V. However, the current of M311/LIG increased more rapidly and reached a higher discharge capacity than M111/LIG, which implies (1) M311/LIG has many more accessible sites and (2) the O<sub>2</sub> diffusion in M311/LIG is better. The enhanced rechargeability of M311/LIG is also demonstrated by the electrochemical impedance spectra (EIS) in **Figure 5.10d** 

(Equivalent circuit shown in **Figure 5.11**). At the 5<sup>th</sup> cycle, M111/LIG exhibited slightly lower cathode charge-transfer resistance ( $R_{CT cathode}$ ) of 241  $\Omega$  than that of M311/LIG (296  $\Omega$ ). The  $R_{CT cathode}$  of M111/LIG increased by 93  $\Omega$  at 35<sup>th</sup> cycle, which is ~60% higher than the increasement of M311/LIG (56  $\Omega$ ). The more increased  $R_{CT}$  cathode suggests the more significant accumulation of undecomposed discharge products on M111/LIG than on M311/LIG. The SEM images of electrode with a discharge capacity of 10 mAh/cm<sup>2</sup> (**Figure 5.12**) also support this hypothesis. The discharge capacity of M311/LIG is 26.3 mAh/cm<sup>2</sup>, and the morphology at 10 mAh/cm<sup>2</sup> demonstrates the continuing growth of discharge products. However, as for M111/LIG electrode, the discharge products cover the surface at 10 mAh/cm<sup>2</sup>. This observation matches the previous result (**Figure 5.2**, **Figure 5.6 and Figure 5.13**) and emphasizes the importance of morphology control of discharge products.



Figure 5.12. SEM images of the (a,b) M111/LIG and (c,d) M311/LIG electrodes at a discharge capacity of 10 mAh/cm<sup>2</sup>.



Figure 5.13. (a,b) TEM images and (c) Fourier-transform infrared spectrum of M311/LIG after discharging.



Figure 5.14. Galvanostatic cycling performance (a) and (b) discharge and charge mid-voltage *vs* cycle number of M111/LIG for Na-air batteries.



Figure 5.15. (a) Galvanostatic cycling performance and (b) discharge and charge mid-voltage *vs* cycle number of M311/LIG for Na-air batteries.

To demonstrate the general function ability of M111/LIG and M311/LIG catalysts, a Na-air battery with those catalysts were also tested in the filtered breathing air environment (**Figure 5.14 and Figure 5.15**). A Na-air battery with M311/LIG catalysts showed a lower charge potential the Na-air battery with M111/LIG, which indicates that the discharge product of M311/LIG is Na<sub>2</sub>O, while M111/LIG leads to the formation of Na<sub>2</sub>O<sub>2</sub>. The 4-electron transfer on M311/LIG accords with the high ORR activity of Mn species in aprotic electrolytes.

### 5.2.3. Conclusion

In this study, we demonstrated the bifunctional catalysts M111/LIG and M311/LIG as efficient and durable cathode catalysts for Li-O<sub>2</sub> batteries. The highest capacity could be reached with M311/LIG at 26.3 mAh/cm<sup>2</sup> at 2.0 V. The batteries also show a reversible cycling performance for >100 cycles with a cutoff capacity of 0.4 mAh/cm<sup>2</sup>. By carefully studying the discharge and charge processes through SEM, XRD and XPS, we found that the difference in elemental composition results in different size distributions of the particles, which further affected the morphology of discharge products in the Li-O<sub>2</sub> battery. These findings could lead to the development of efficient bifunctional catalysts for metal-O<sub>2</sub> batteries and further highlight the importance of tailoring the internal morphology of a metal-O<sub>2</sub> battery towards an excellent cycling stability.

## **5.3. Experimental Contributions**

**Muqing Ren** designed the experiments, prepared the samples, and conducted part of the characterizations including SEM, TEM, Raman, XPS, electrochemical measurements, battery test. Jibo Zhang designed part of the experiments and conducted part of the characterizations including, electrochemical measurements, SEM and XRD.

## Chapter 6

# Quasi-Solid-State Li-O<sub>2</sub> Batteries with Laser-Induced Graphene Cathode Catalysts

This chapter was entirely copied from reference 261.

### **6.1. Introduction**

The increasing demand for energy resources encourages the development of high energy density storage systems. During recent years, Li-O<sub>2</sub> batteries are attracting considerable interest due to their outstanding theoretical capacities and energy densities. Combining the Li metal anode with O<sub>2</sub> as the cathode, a Li-O<sub>2</sub> battery can, in principle, deliver a specific energy density of ~3500 Wh/kgLi<sub>2O2</sub>, which is several times higher than conventional Li-ion batteries (LIBs). Since the first demonstration of a rechargeable Li-O<sub>2</sub> battery by Abraham and Jiang in 1996,<sup>262</sup> an improved rechargeable Li-O<sub>2</sub> battery was presented by Bruce and coworkers in 2006.<sup>263</sup> The applicability of a delicately designed air cathode was then illustrated, and studies on non-aqueous Li-O<sub>2</sub> batteries have ensued.<sup>157, 217, 226, 264-267</sup> The use of metallic Li and liquid electrolytes in Li-O<sub>2</sub> batteries has introduced the same issues found in LIBs, such as electrolyte leakage, poor stability, flammability and volatility of the electrolyte, and Li dendrite growth.<sup>268-272</sup> The sluggish oxygen electrochemistry at the O<sub>2</sub> cathode contributes to additional problems, including the accumulation of discharge products and blockage of O<sub>2</sub> diffusion.<sup>273, 274</sup> Moreover, the intermediate oxygen radical anion, superoxide (O<sub>2</sub>-) formed during the reduction process is active in decomposing the organic carbonate electrolyte and presents a challenge when using conventional electrolytes.<sup>275,276</sup>

The use of solid-state electrolytes over liquid electrolytes has been considered as an efficient method to overcome the safety issues caused by organic solvents. The well-studied inorganic solid electrolytes, including lithium superionic conductors such as garnets,<sup>277</sup> exhibit stable potential window and high ionic conductivity for Li-O<sub>2</sub> electrochemistry. However, poor interfacial properties raise the interface impedance and block ionic transport, which is essential for the cathode reactions, since Li<sub>2</sub>O<sub>2</sub> has very low Li<sup>+</sup> ionic and electronic conductivities.<sup>278, 279</sup> Although recently developed sulfide-based compounds have demonstrated high ionic conductivity and modulus as solid electrolytes, they exhibit high sensitivity to O<sub>2</sub> and moisture.<sup>280-285</sup> Alternatively, polymer gel electrolytes (PGEs) might provide a better electrolyte-electrode interface due to their viscoelasticity and low

modulus.<sup>286</sup> Moreover, PGEs were developed to improve the ionic conductivity and solvation of Li<sup>+</sup> while maintaining a relatively high mechanical strength.<sup>287</sup> Yet, when considering incorporation of PGEs with the O<sub>2</sub> cathode, the high charging potential (due to the high overpotential of O<sub>2</sub> electrochemistry) would not only challenge the anodic stability of the electrolytes, but also diminish the energy efficiency of the Li-O<sub>2</sub> battery. The incorporation of a redox mediator, for example, LiI, InI<sub>3</sub> and tetrathiafulvalene, into the electrolytes could facilitate the decomposition of Li<sub>2</sub>O<sub>2</sub> and lower the charge potential, at the possible cost of migration of the redox mediator towards the anode and subsequent passivation of Li anode.<sup>175, 229, 288-290</sup> Therefore, a careful consideration of the overall design and components of the Li-O<sub>2</sub> battery is necessary when considering the use of PGEs.

We demonstrate a strategy towards practical Li-O<sub>2</sub> batteries using a dual polymer gel electrolyte (DPGE) with an efficient MnO<sub>2</sub>/laser-induced graphene (LIG) cathode catalyst. In this design, the commericially available poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) was used as the backbone of the DPGE to provide mechanical stability. Trimethylolpropane ethoxylate triacrylate (TEMPT) was UV-polymerized *in situ* inside the PVDF-HFP network, providing a high ionic (Li<sup>+</sup>) conductivity due to abundant ethylene oxide moieties efficiently solvate Li<sup>+</sup> ions in the gel electrolyte. The DPGE demonstrated high stability through a >2000 h Li plating/stripping process without short-circuiting or increasing the interfacial resistance. The DPGE was further combined with the recently developed method of direct laser writing catalysts to enable a practical Li-O<sub>2</sub> battery with a metallic Li anode. The direct laser writing catalysts show promising properties, such as high porosity, high electrical conductivity and chemical stability, all of which are conducive to the development of porous materials for efficient cathode catalysts with high surface area and stable architecture. The MnO<sub>2</sub>/LIG catalyst was selected in this work for its high catalytic activity towards oxygen reduction/evolution reactions (ORR/OER). MnO<sub>2</sub>/LIG demonstrated its high activity as the cathode material for quasi-solid-state Li-O<sub>2</sub> battery. The battery with DPGE and a MnO<sub>2</sub>/LIG cathode catalyst shows stable galvanostatic charge/discharge performance for >200 cycles with a cut-off capacity of 0.4 mAh/cm<sup>2</sup>. Furthermore, the cell sustained a high capacity of 2.0 mAh/cm<sup>2</sup> over 50 cycles at an elevated current density of 0.4 mA/cm<sup>2</sup>, while the charging potential was lower than 4.5 V (vs Li<sup>+</sup>/Li). The results prove the applicability of combining quasi-solid-state electrolytes with catalytic O<sub>2</sub> cathodes for high-reversible-capacity Li-O<sub>2</sub> batteries. The combination of DPGE with direct laser writing processed noble-metal-free catalysts contribute a new direction to the development of practical Li-O<sub>2</sub> batteries.

## 6.2. Quasi-Solid-State Li-O<sub>2</sub> Batteries with Laser-Induced Graphene Cathode Catalysts

6.2.1. Experimental Section

6.2.1.1. Material Synthesis

### **Preparation of the catalyst**

All samples were prepared under ambient air. Kapton<sup>®</sup> PI films (McMaster-Carr, Cat. No. 2271K3, thickness: 0.005") were used as received. LIG was generated by a CO<sub>2</sub> laser (10.6  $\mu$ m, Universal XLS10MWH laser cutter platform) on the PI film in air using 3% of full power and 5% of full speed with an image density of 6. The LIG was patterned on PI as a 2×2 cm<sup>2</sup> square.

1 M MnSO<sub>4</sub> solution was prepared with deionized water. The as-prepared LIG  $(2 \times 2 \text{ cm}^2)$  was treated by the O<sub>2</sub> plasma (Boekel Model 135500) for 1 min to increase the hydrophilicity. 80 µL of the solution were dropped onto the LIG. The soaked LIG (on PI) was dried in air at room temperature overnight and then under vacuum (~120 mm Hg). Then the LIG was lased again atop the previous LIG pattern under the same conditions (3% of full power and 5% of full speed with an image density of 6). Then the powder was scratched from the PI and collected for further characterization. For comparison, the MnO<sub>2</sub>/LIG catalysts prepared from different precursor concentrations, including 0.1 M and 2 M MnSO<sub>4</sub>, were synthesized using a similar method. The control LIG was prepared similarly without adding the MnSO<sub>4</sub>.

#### **Preparation of the DPGE**

To a solution of 2.0 g PVDF-HFP in 8 g NMP was added 8 mL 1 M LiTFSI/TEGDME. The mixture was stirred for 5 min. Then 0.02 g HMPP and 6 g TEMPT were added to the solution. The mixture was stirred for 5 min, and then cast on a glass substrate and irradiated with a 365 nm UV lamp for 30 s to obtain a DPGE film.

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### 6.2.1.2. Materials characterization

### **Materials characterization**

SEM images were obtained by a FEI Quanta 400 high-resolution field emission SEM. TEM images measurements were carried out at 80 keV using a FEI Titan Themis3 S/TEM equipped with image and probe spherical aberration correctors. XPS was done by a PHI Quantera SXM scanning X-ray microprobe with a monochromatic 1486.7 eV Al KR X-ray line source, 45° take off angle, and a 200 µm beam size. Raman spectroscopy was performed at 532 nm laser excitation. TGA was performed on a Q-600 Simultaneous TGA/DSC (TA Instrument). The sample was heated to 1000 °C in air.

### **Electrochemical measurements**

Electrochemical measurements were obtained on a rotating disk electrode (5 mm dia., Pine Research Instrumentation). For the preparation of working electrode, 4 mg of the catalyst and 80  $\mu$ L of 5 wt% Nafion solution were mixed in 1 mL water/ethanol (4/1, v/v) followed by 2 h bath-sonication (Cole Parmer, model 08849-00) to form a homogeneous ink. Then 12  $\mu$ L of the catalyst ink was dropped onto the glassy carbon electrode, and dried under vacuum (~120 mmHg) at room temperature (The catalyst loading is ~0.265 mg/cm<sup>2</sup>). The electrochemical measurements were carried out in a 3-electrode configuration using CHI 608D and VMP3 (Bio-Logic Co.) electrochemical workstation. For OER test, a Pt plate and Hg/HgO (in 1 M KOH) were used as the counter and reference electrode,

respectively. For ORR test, a graphite rod and Hg/HgO (in 1 M KOH) were used as the counter and reference electrode, respectively. The tests regarding oxygen evolution were done in 0.1 M KOH with 95% iR compensation. The potential is normalized with RHE.

For the OER test, the scan rate of the working electrode was 5 mV/s with a rotating speed of 1600 rpm. The number of electrons transferred (*n*) during ORR was calculated by the Koutecky-Levich (K-L) equation according the LSV curves with varying rotating speed from 225 to 1600 rpm.

### **Battery test**

The electrochemical performance of MnO<sub>2</sub>/LIG bifunctional catalysts and solid electrolyte DPGE was tested in lithium-oxygen cells through coin type CR2032 cells. All the cells were assembled in the glove box under an argon atmosphere. The Li<sup>+</sup> transference number is measured using the potentiostatic polarization from a coin cell, in which the DPGE is sandwiched by two pieces of Li foil.<sup>291</sup> A small potential (5 mV) was applied on the cell and the current density was monitored. The transference number was determined by the ratio of the stabilized current to the initial current. The CR2032 Li-oxygen cell includes the Li foil, as-prepared DPGE, and the O<sub>2</sub> cathode electrode. The cathode was prepared by casting a slurry that consists of 80 wt% catalysts, 10 wt% Super P (TIMCAL) and 10 wt% PVDF (Alfa Aesar) in NMP on a piece of carbon paper. The galvanostatic discharge/charge tests were carried out in voltage range of 2.0 to 5.0 V (*vs* Li/Li<sup>+</sup>).



Figure 6.1. (a) Preparation and characterization of the DPGE. The figure shows the films that can be made by this approach. (b) Cross-section and (c) top-view SEM images of the DPGE. (d) Li<sup>+</sup> transference number determination. Inset shows the impedance spectra of the DPGE.

The synthesis of the DPGE was assisted by UV-activating polymerization of TEMPT with PVDF-HFP as the backbone as shown in **Figure 6.1a**. Briefly, PVDF-HFP was dissolved in *N*-methyl-2-pyrrolidinone (NMP). This solution was mixed with lithium bistrifluoromethanesulfonimidate/tetraethylene glycol dimethyl ether (LITFSI/TEGDME). After adding 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP, photo-initiator) and TEMPT to the solution, it was cast on top of a glass substrate and cured with UV irradiation. The DPGE obtained through this method was semi-

transparent with a typical thickness of  $\sim 287 \,\mu m$  (Figure 6.1b) by scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) results shown in Figure 6.3 demonstrates the distribution of Li<sup>+</sup> in the polymer network. Figure 6.1c displays the cross-sectional morphology of DPGE that exhibits a dense structure, indicating the well-formed interpenetrating polymer network between PVDF-HFP and PEG. The broad and weak diffraction peak in Figure 6.4 suggests there is no significant aggregation/crystallization of PVDF-HFP or PEG in the DPGE. The slightly rough surface may be beneficial for interfacial contact with the  $O_2$  cathode, as it provides a high active surface with the cathode catalysts to facilitate the Li<sup>+</sup> transportation. The Li<sup>+</sup> transference number  $(t_{Li+})$  and conductivity of the DPGE is summarized in **Figure 6.1d**. The DPGE exhibits a high  $t_{Li+}$  of 0.6 and a total conductivity of 3.25×10<sup>-4</sup> S/cm at room temperature, which are comparable to the liquid electrolytes. The electrolyte's electrochemical potential window is a critical factor to ensure Li-O<sub>2</sub> battery cycling reversibility. Therefore, linear sweep voltammogram (LSV) testing was carried out on a Li/DPGE/stainless steel cell to test DPGE's anodic stability between 2.0-5.0 V as shown in Figure 6.5. No obvious decomposition was observed before the voltage reaches 4.7 V, which demonstrates the chemical stability of DPGE in withstanding a high oxidation potential. A Li/DPGE/Li cell was fabricated to examine the compatibility of the DPGE with metallic Li. As shown in Figure 6.6, no short-circuit or build-up of interfacial resistance was observed after a 2000 h galvanostatic test.

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Figure 6.2. Preparation of the MnO<sub>2</sub>/LIG Catalysts.



Figure 6.3. XPS spectra of the DPGE in (a) C 1s, (b) Li 1s, (c) F 1s and (d) O 1s regions.



Figure 6.4. XRD pattern of the DPGE.



Figure 6.5. Anodic stability of the DPGE.



Figure 6.6. Voltage stability of batteries with DPGE at 0.07 mA/cm<sup>2</sup> (discharge 1 h and charge 1 h).



Figure 6.7. Characterization of the  $MnO_2/LIG$  catalyst. (a-c) SEM images and (d-f) high resolution TEM images of  $MnO_2/LIG$ .

Because of to the sluggish  $O_2$  electrochemistry at the  $O_2$  cathode, an efficient bifunctional catalyst is desired to lower the overpotentials in both discharge and charge process. Instead of incorporating redox mediators (RMs, also known as soluble homogeneous catalysts in aprotic Li-O<sub>2</sub> batteries) in the electrolytes, we proposed to use a porous heterogeneous catalyst at the cathode to avoid possible "cross-talk" between Li and RMs. MnO<sub>2</sub> has shown high activity and durability in electrocatalysis and therefore was selected as the cathode catalyst for our study. The in situ synthesis of MnO<sub>2</sub>/LIG catalysts was done by a re-lasing method as previously reported (**Figure 6.2**).<sup>70, 114</sup> PI is lased to make LIG, then exposed to an oxygen plasma to increase the hydrophilicity. An aqueous solution of the MnSO<sub>4</sub> is applied and then the LIG re-lased under the same conditions. The MnO<sub>2</sub>/LIG is then scraped from the PI surface to afford the active catalytic material. The morphology structure of MnO<sub>2</sub>/LIG catalyst was characterized by SEM (Figure 6.7a-c). The SEM images show that the typical porous structure of LIG was maintained after MnO<sub>2</sub> was in situ grown by direct laser writing. Additionally, there is no obvious aggregation of MnO<sub>2</sub> nanoparticles found on the LIG, indicating the homogeneous distribution of nanoparticles. The 3D porous structure will benefit the diffusion of O<sub>2</sub> to the active catalyst, which also benefits contact between the electrode and DPGE. The LIG will contribute to a high discharge capacity since the capacity is determined by the porous cathode catalyst structure's ability to accommodate the accumulation of discharged products.<sup>292, 293</sup>
Transmission electron microscope (TEM) images demonstrate that MnO<sub>2</sub> nanoparticles were homogeneously distributed on the graphene as shown in **Figure 6.7d-f.** The nanoparticles exhibit a uniform size distribution of  $\sim 10$  nm. The inset high resolution TEM (HRTEM) image reveals that the lattice spacing of  $MnO_2$  is ~ 0.24, 0.30 and 0.49 nm, respectively. These values correspond to the interplane spacing of the (211), (310) and (200) planes of  $\alpha$ -MnO<sub>2</sub> (PDF44-0141), which is in accordance with the X-ray diffraction (XRD) data (Figure 6.8a). It further confirms the formation of  $MnO_2$  nanoparticles embedded on graphene structures. The multilayer graphene structure arranged around the metal oxides is consistent with the Raman data (Figure 6.8b). The results confirm that the nanoparticles and LIG were formed during the direct laser writing. Figure 6.8a shows the crystalline structure of the catalysts. The characteristic peak of LIG is observed at 25.6°, corresponding to the multilayer graphene structure. The crystal planes of (200), (310), (211), (301) and (510) are well-defined from the XRD pattern and match the lattice spacing of  $\alpha$ -MnO<sub>2</sub>. The intensities of these peaks are relatively weak, which may be caused by the small size of the crystalized nanoparticles and rapid coverage

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of LIG on the surface of  $MnO_2$ .

The Raman active mode located at 643 cm<sup>-1</sup> in **Figure 6.8b** is attributed to the symmetric stretching vibration (Mn-O) of the MnO<sub>6</sub> octahedron. This result is consistent with the XRD evidence that MnO<sub>2</sub> is the primary phase of manganese species in the catalyst. The clearly identified D, G and 2D peaks suggest the existence of defective or bent multi-layer graphene as the characteristic sign of LIG.



Figure 6.8. Characterization of the MnO<sub>2</sub>/LIG catalyst.

# (a) Powder XRD pattern and (b) Raman spectra of MnO<sub>2</sub>/LIG. (c) XPS survey of MnO<sub>2</sub>/LIG and (d) high-resolution spectrum of Mn 2p region.

The elemental composition and chemical valence state were analyzed by X-ray photoelectron spectroscopy (XPS). A XPS survey spectrum of the MnO<sub>2</sub>/LIG catalyst illustrates characteristic Mn, O and C species (**Figure 6.8c**). **Figure 6.8d** presents the high-resolution XPS spectrum in the Mn 2p region for the MnO<sub>2</sub>/LIG catalyst. It has spin-orbit split peaks of Mn 2p<sub>3/2</sub> and 2p<sub>1/2</sub> at 642.1 and 653.8 eV, respectively. The spin-energy separation is 11.7 eV, which suggests the existence of Mn<sup>4+</sup> species.

The O 1s spectra shows a broad peak with binding energy centering at ~532 eV, which is attributed to cumulative signal of Mn oxides and the oxygen-containing moieties such as C-O and C=O from LIG (**Figure 6.9a**). Thermogravimetric analysis (TGA) shows that the weight percent of Mn is 17.9% in MnO<sub>2</sub>/LIG (**Figure 6.9b**).



Figure 6.9. (a) XPS spectra of O 1s region in MnO<sub>2</sub>/LIG catalyst. (b) TGA of the pristine and MnO<sub>2</sub>/LIG. And the contact angle of the (c) pristine LIG (on PI film), and (d) as prepared MnO<sub>2</sub>/LIG (on PI film).



Figure 6.10. Electrochemical characterization of the MnO<sub>2</sub>/LIG catalyst.

(a) LSV curves for ORR at different rotation speeds in O<sub>2</sub>-saturated 0.1 M KOH and (b) corresponding K-L plots of MnO<sub>2</sub>/LIG. (c) OER polarization curve of MnO<sub>2</sub>/LIG and (d) the corresponding Tafel plots.

The ORR and OER activities of the MnO<sub>2</sub>/LIG catalysts were assessed in 0.1 M KOH using a 3-electrode configuration. Although the O<sub>2</sub> electrochemistry in aqueous electrolyte is different from that in aprotic electrolytes, the results may still provide desirable guidance towards the application in Li-O<sub>2</sub> batteries. **Figure 6.10a** shows

the rotating-disk-electrode voltammograms for ORR of MnO<sub>2</sub>/LIG electrode at different rotation speeds. The Tafel slope of 101 mV dec<sup>-1</sup> suggests favorable kinetics of ORR on MnO<sub>2</sub>/LIG (Figure 6.11). These data show characteristic increasing diffusion-limited current densities with higher rotation speeds. The electron transfer number (n) was evaluated according to the Koutecky-Levich (K-L) eq (Experimental Section) and the results are plotted in Figure 6.10b. In the potential window (0.25-0.55 V vs RHE), the average n for MnO<sub>2</sub>/LIG is ~ 4.0, suggesting a predominantly direct four-electron transfer process. These results demonstrate the strong affinity of the MnO<sub>2</sub> surfaces to O<sub>2</sub>, which is a key procedure of O<sub>2</sub> reduction in aprotic electrolyte. Figure 6.10c shows the OER performance of MnO<sub>2</sub>/LIG. The onset potential is  $\sim$ 1.5 V, corresponding to an overpotential of 270 mV. The Tafel slope is  $\sim 148$  mV/dec (Figure 6.10d) and the potential to reach 10 mA/cm<sup>2</sup> is 1.85 V. The effect of precursor concentration on the morphology and the activity of MnO<sub>2</sub>/LIG catalyst was investigated (Figure 6.12 and Figure 6.13). It is concluded that a moderate loading of nanoparticles on LIG could assure a uniform distribution of the active sites to avoid aggregation and maximize their ability to deliver a high mass activity. The control LIG exhibited much lower performance than MnO<sub>2</sub>/LIG in ORR and OER, suggesting a small contribution from the LIG structure on the intrinsic catalytic activity (Figure 6.14). The MnO<sub>2</sub>/LIG exhibits comparable performance to the Mn based catalysts synthesized by conventional methods (Table 6.1 and Table 6.2), demonstrating the effectiveness and reliability of the LIG method for the facile preparation of catalysts. The nano- and meso-porous

structure from LIG lead to higher surface area and better conductivity whereas the uniform distribution of nanosized MnO<sub>2</sub> particles provides abundant surface active sites towards the O<sub>2</sub> electrochemical process in a Li-O<sub>2</sub> battery. Based on MnO<sub>2</sub>/LIG activity toward both OER and ORR performance, it was further applied in a quasisolid-state Li-O<sub>2</sub> battery to enhance the cycle reversibility and to study the mechanism.



Figure 6.11. The Tafel plots of MnO<sub>2</sub>/LIG for ORR.





Figure 6.12. TEM images of MnO<sub>2</sub>/LIG catalyst prepared from precursor solution with different concentrations of MnSO<sub>4</sub>: (a) 0.1 M and (b) 2 M.

Figure 6.13. The effect of the precursor concentration on the electrochemical performance of MnO<sub>2</sub>/LIG.

LSV curves for ORR at different rotation speeds in O<sub>2</sub>-saturated 0.1 M KOH and corresponding K-L plots of MnO<sub>2</sub>/LIG synthesized from different concentrations of MnSO<sub>4</sub>: (a, c) 0.1 M; (b, d) 2 M And the comparison of (e) ORR and (f) OER polarization curves of the MnO<sub>2</sub>/LIG catalysts at 1600 rpm.



Figure 6.14. The electrochemical performance of control LIG.

(a) ORR and (b) OER polarization curves of control LIG and  $MnO_2/LIG$  in  $O_2$ -saturated 0.1 M KOH at 1600 rpm. (c) ORR LSV curves at different rotation speeds in  $O_2$ -saturated 0.1 M KOH and (d) corresponding K-L plots of control LIG.

Catalyst	Preparation alyst method		Overpotential (mV)	Tafel slope (mV/dec)	Ref
MnO <sub>2</sub> /LIG	LIG	0.88	350	101	This work
Ag- MnO <sub>2</sub> /graphene	Thermal annealing	0.068 (Hg/HgO)	N/A	86	294
CNT-graphene- MnO <sub>2</sub> nanowires	Hydrothermal and thermal annealing	0.88	350	69	295
Ni/a-MnO <sub>2</sub>	Solid state method	0.87	360	N/A	296
MnO <sub>2</sub> /RGO	Chelation mediated aqueous method	0.02 V (Ag/AgCl)	N/A	N/A	297
MnO <sub>2</sub> /C	Precipitation	0.85	280	115	298
NiO/MnO2@PANI	Inverse micelle templating	0.92	310	124	244
NiO/MnO <sub>2</sub>	MnO <sub>2</sub> Inverse micelle templating		330	197	244
0.7%Cu@NG-750	Thermal annealing	0.83	400	N/A	299

## Table 6.1. Brief comparison of the ORR performance of Mn based catalysts.



Figure 6.15. Cycling performance of quasi-solid-state Li-O<sub>2</sub> battery.

(a) First-cycle discharge and charge profile of the  $MnO_2/LIG$  electrode at various current densities. (b) Rate performance of  $MnO_2/LIG$  electrode. (c) First-cycle discharge and charge performance of the  $MnO_2/LIG$  electrode at a current density of 0.4 mA/cm<sup>2</sup> with limited capacity of 2 mAh/cm<sup>2</sup>. (d) Discharge and charge mid-voltage vs cycle number at a current density of 0.4 mA/cm<sup>2</sup> with limited capacity of 2.4 mA/cm<sup>2</sup>.

Catalyst	Preparation method	Onset E	$\eta_{10}$	Tafel slope	Ref
		(V)	(mV)	(mV/dec)	
MnO <sub>2</sub> /LIG	LIG	1.5	620	148	This
					work
Ni/α-MnO <sub>2</sub>	Solid State reaction	1.62	510	107.4	<u>296</u>
Graphene-Mn-	Hydrothermal and	1.56	N/A	371.3	<u>300</u>
NiCo	thermal annealing				
Co <sub>3</sub> O <sub>4</sub> -MnO <sub>2</sub> -CNT	Thermal annealing and	1.65	510	54	<u>301</u>
	acid treatment				
Mesoporous	Nanocasting method	1.56	520	51	<u>147</u>
Co <sub>3</sub> O <sub>4</sub>					
MnO <sub>2</sub> -CoFe <sub>2</sub> O <sub>4</sub> /C	Solvothermal and	1.56	470	130	<u>302</u>
	precipitation				
MnO <sub>2</sub> /C	Solvothermal and	1.56	550	227	<u>302</u>
	precipitation				
ZnCo	Co-precipitation	1.56	430	73	<u>151</u>
LDH/graphene					
dandelion-like $\alpha$ -	Solvothermal	1.62	550	155	303
MnO <sub>2</sub>					
MnxCo <sub>3-x</sub> O <sub>4-δ</sub>	Self-templating	1.52	350	85	<u>149</u>
NiCo LDH	Solvothermal	1.52	420	113	<u>150</u>
nanosheets					

### Table 6.2. Brief comparison of the OER performance of Mn based catalysts.

To explore the potential application of the bifunctional catalysts MnO<sub>2</sub>/LIG and solid electrolyte DPGE in Li-O<sub>2</sub> batteries, the cells were tested through galvanostatic discharge and charge processes. The typical Li-O<sub>2</sub> coin cell configuration consists of a Li foil as the anode, a piece of DPGE as the separator and MnO<sub>2</sub>/LIG as the cathode catalyst, and dry O<sub>2</sub> is maintained during the test as the cathode. Figure 6.15a shows the representative first discharge and charge voltage profiles for the MnO<sub>2</sub>/LIG electrode at various current densities with time limited to 5 h. The first cyclic voltage gap is 0.92 V when the current density is 0.08 mA/cm<sup>2</sup>; this voltage gap increased to 1.34 V at a current density of 0.4 mA/cm<sup>2</sup> (voltage gap refers to the difference between charge and discharge voltage value at half the cut-off capacity). Notably, the current density increased from 0.08 to 0.4 mA/cm<sup>2</sup>, the discharge potential decreased very little, which indicates the intrinsically high activity (high exchange current) of the MnO<sub>2</sub>/LIG towards the oxygen reduction in aprotic electrolyte. During the charge process, the battery exhibited a gradually increasing potential for decomposing the discharge products as the capacity increased, despite the current density. This phenomenon could be understood by the accumulation of discharge products during the discharge process. The discharge products would occupy the most active/accessible sites at the initial step of discharging, then the sites with slightly lower activity would be accessed. Therefore, the former ones were preferentially decomposed at lower overpotential in the charge process. If there is heterogeneous precipitation of the discharge products during the discharge

process (*e.g.* the accumulation of discharge products on the sites that are already covered), the charge process would exhibit a high overpotential even at the beginning due to the low electronic/Li<sup>+</sup> conductivity of the products, namely Li<sub>2</sub>O<sub>2</sub>, LiOH or both.

Figure 6.15b shows the rate performance of MnO<sub>2</sub>/LIG electrode for quasisolid-state Li- $O_2$  battery (0.08 mA/cm<sup>2</sup> - 0.4 mA/cm<sup>2</sup>) with a step current density of 0.08 mA/cm<sup>2</sup>. At each representative current density, the battery was tested for five cycles. It is observed that the charged voltage potential gradually increased while the discharged voltage potential gradually dropped with the increased current densities. This could be attributed to the accumulation of insulating discharge product that results in higher overpotential and decomposition, and the increasing difficulty for O<sub>2</sub> to diffuse through the discharged products to react with Li ions. The battery was discharged and charged for  $\sim 200$  cycles at the current density of 0.08  $mA/cm^2$ . The MnO<sub>2</sub>/LIG electrode for Li-O<sub>2</sub> battery with a conventional Celgard separator and liquid electrolyte (1 M LiTFSI/TEGDME) was also tested at the current density of 0.08 mA/cm<sup>2</sup> for comparison (**Figure 6.16**). Although the battery shows a lower discharge-charge overpotential at the 1<sup>st</sup> cycle, its charging potential increased quickly with cycling. The charging potential reached over 4.5 V at the 80<sup>th</sup> cycle. The quasi-solid-state Li-O<sub>2</sub> battery with DPGE can be recharged for more times than with the conventional liquid electrolyte. The  $\alpha$ -MnO<sub>2</sub> is intrinsically active for O<sub>2</sub> electrochemistry in aprotic Li-O<sub>2</sub> batteries.<sup>304-306</sup> The improved cycling durability with DPGE further highlights the importance of a stable electrolyte

system for a practical Li-O<sub>2</sub> battery. **Figure 6.15**c and d show the battery's cyclic performance under a large current density of 0.4 mA/cm<sup>2</sup>. The cells can be cycled  $\sim$  50 times with the cut-off capacity of 2 mAh/cm<sup>2</sup> without significant increase of the overpotentials (





Figure 6.16. Testing with a traditional Celgard separator.

(a) Discharge and charge voltage profiles of the MnO<sub>2</sub>/LIG electrode and (b) rate performance of MnO<sub>2</sub>/LIG electrode for Li-O<sub>2</sub> battery with 1 M LiTFSI/G4 at a current density of 0.08 mA/cm<sup>2</sup>.

Electrolyte type	Polymer backbone	Temp. (°C)	Gas	Current density/ Cut-off capacity	Cycle	1 <sup>st</sup> cycle mid-V	Ref.
liquid electrolyte + solid electrolyte	PVDF-HFP	50	02	0.25 mA/cm <sup>2</sup> (10 mAh)	30	4.2	307
gel electrolyte	PVDF-HFP	N/A	02	50 mA/g (500 mAh/g)	50	3.9	308
gel electrolyte	PVDF-HFP	25	02	0.05 mA/cm <sup>2</sup> (500 mAh/g)	40	4.5	309
gel electrolyte	PVDF-HFP	30	02	200 mA/g (500 mAh/g)	100	3.8	310
gel electrolyte	PVDF-HFP	N/A	02	0.125 mA/cm <sup>2</sup> (500 mAh/g)	54	4.2	311
gel electrolyte with additive (aluminum- doped lithium lanthanum titanate (/m- SiO <sub>2</sub> )	PVDF-HFP	N/A	02	0.1 mA/cm <sup>2</sup> (1000 mAh/g)	71	3.6	312
gel electrolyte	PVDF-HFP	N/A	air	1000 mA/g (1000 mAh/g)	90	3.8	313
DPGE	PVDF-HFP	25	02	0.08 mA/cm <sup>2</sup> (0.4 mAh/cm <sup>2</sup> ) 86 mA/g (430 mAh/g)	200	3.64	This work
DPGE	PVDF-HFP	25	02	0.4 mA/cm <sup>2</sup> (2.0 mAh/cm <sup>2</sup> ) 430 mA/g (2150 mAh/g)	50	3.94	This work

Table 6.3. Comparison of the Li-O<sub>2</sub> solid state battery with other PVDF-HFP based solid state batteries.



Figure 6.17. Morphological characterization of (a) discharged  $MnO_2/LIG$  electrode (10 mAh cm<sup>-2</sup>) and (b) charged  $MnO_2/LIG$  electrode. (c) XRD characterization of  $MnO_2/LIG$  electrode. (d) Li 1s XPS of the  $MnO_2/LIG$  electrode.

The morphology and crystal structure change of the electrode were investigated through SEM, XRD and XPS characterizations, which help to further understand the reaction process inside the quasi-solid-state Li-O<sub>2</sub> battery. Small crystal particles were formed when the MnO<sub>2</sub>/LIG electrode was discharged for 125 h (10 mAh cm<sup>-2</sup>, **Figure 6.17**a), and the particles were decomposed after being charged back for 125 h, (**Figure 6.17**b). **Figure 6.17**c demonstrates the crystalline structure of the MnO<sub>2</sub>/LIG electrode after discharge (125 h) and charge (125 h). The

characteristic peak of multilayer graphene (LIG, 25.6°) was maintained during the discharge and charge. The discharge products are identified as LiOH and Li<sub>2</sub>O<sub>2</sub>. Li<sub>2</sub>O<sub>2</sub> is produced from the successive reduction of  $O_2$  to  $O^{2-}$  and  $O_2^{2-}$ . LiOH is formed through several possible pathways, *e.g.* reaction with a trace amount of  $H_2O$  on the surface of the DPGE that might come from the air during the DPGE synthesis, moisture in the O<sub>2</sub>, and reaction of superoxide with the PVDF binder. From a previous study, it was found that Mn species facilitate the decomposition of  $H_2O_2$ and move the reaction forward to result in the formation of LiOH.<sup>255</sup> Despite the dual discharge products, the catalysts could facilitate the decomposition process and enhance the cycling stability. During the charge process, all of the discharged Li<sub>2</sub>O<sub>2</sub> and LiOH was decomposed. Figure 6.17d illustrates the Li 1s XPS survey corresponding to the electrode discharged (125 h) and then charged (125 h) states. The Li 1s XPS has a main peak at  $\sim$  54.4 eV, which is ascribed to Li<sub>2</sub>O<sub>2</sub> and LiOH. Li<sub>2</sub>O<sub>2</sub> and LiOH have the same Li 1s binding energy and it is difficult to distinguish those two from XPS characterization.

In our previous study on Li-O<sub>2</sub> batteries with glyme-based electrolytes,<sup>202</sup> we found that the surface active sites are of great importance in modulating the size and distribution of discharge products. Because of the low donor number of glymes and high O<sub>2</sub> solubility in electrolyte (*e.g.* 0.6 mM in 1 M LiTFSI/G4), the nucleation process of LiO<sub>2</sub> highly depends on the accessible sites on the cathode/electrolyte interface. Similarly, in the quasi-solid-state Li-O<sub>2</sub> battery, where the O<sub>2</sub> electrochemical reactions take place at the electrolyte/electrode surface, a high

density of accessible sites is a necessity for a high reversible capacity. Otherwise, the discharge products would fill the sites and lead to either high overpotentials for  $Li^+/e^-$  conduction and/or blockage of O<sub>2</sub>. Another key factor is the compatible interfacial contact between solid electrolyte and cathode. The intrinsic viscoelasticity and low modulus of the polymer-based quasi-solid electrolyte would alleviate the interfacial tension and possible loss of conductive contact due to volume change through cycling. Therefore, we suggest the use of porous cathode catalysts with the solid electrolytes for practical Li-O<sub>2</sub> batteries. The utilization of quasi-solid electrolyte has minimized the utilization of liquid electrolyte, the latter of which is unstable against superoxide as well as high anodic potentials. The incorporation of efficient cathode catalyst further lowers the overpotentials and enables a long cycle life of the batteries. However, although the t<sub>Li+</sub> of the DPGE is higher than the liquid electrolytes, the overall Li<sup>+</sup> conductivity is still lower than that of the liquid electrolytes, which could lead to high overpotentials under high current densities. Hence, future optimization should be focused on improving the t<sub>Li+</sub> and Li<sup>+</sup> conductivity, as well as the activity of the cathode catalyst.

#### 6.2.3. Conclusion

In this study, we demonstrated a quasi-solid-state Li-O<sub>2</sub> battery with DPGE as the separator and solid-phase synthesized bifunctional catalyst MnO<sub>2</sub>/LIG as cathode catalyst. Benefiting from the intrinsic high activity of LIG and stability of the DPGE, the Li-O<sub>2</sub> battery demonstrated enhanced performance in cycling life. The quasi-solid-state battery cycled ~200 times with a cut-off capacity 0.4 mAh/cm<sup>2</sup> and cycled ~50 times with a high cut-off capacity 2.0 mAh/cm<sup>2</sup> at a high current density of 0.4 mA/cm<sup>2</sup>. The results here suggest that further developments in carbon-metal oxide composite cathodes are warranted in the quest to fabricate Li-O<sub>2</sub> batteries with markedly higher energy density than most current commercial systems.

#### 6.3. Experimental Contributions

**Muqing Ren** designed the experiments, prepared the samples, and conducted part of the characterizations including SEM, TEM, Raman, XPS, electrochemical measurements, battery test. Jibo Zhang designed part of the experiments and conducted part of the characterizations including, electrochemical measurements, SEM and XRD.

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