



## Short communication

## Electrochemical evaluation of carbon nanotubes and carbon black for the cathode of Li–air batteries



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## HIGHLIGHTS

- Demonstrates the role of carbon on ORR and OER kinetics for Li/air batteries.
- SWCNT had the highest peak current density per gram for ORR and OER.
- SWCNT has a similar onset potential than Au and higher performance.

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## ABSTRACT

Cyclic Voltammetry (CV) was used to screen carbon catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) performance as electrodes for the Li–air battery. Lithium bis(trifluoromethylsulfonyl)imide ( $\text{LiTF}_2\text{N}$ ) in tetraethylene glycol dimethyl ether (TEGDME) was used as the electrolyte during testing. The effect of manganese/manganese oxide addition on the performance of the carbons was compared to that of the bare carbons in a cycling study. From CV results, it was found that single walled carbon nanotubes (SWCNT) had the highest peak current density per gram for ORR and OER than the other types of carbon studied. The SWCNT ORR peak decreased 49% after 100 cycles and only 36% when manganese/manganese oxide was added. The high activity of SWCNT with manganese/manganese oxide spheres make it a desirable material to use as the cathode for Li–air batteries.

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## 1. Introduction

Electrocatalysts are being considered for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) to enhance the discharge/charge reaction kinetics and cyclability for Li–air battery. Several groups working on the electrocatalyst selection have reported similar discharge voltages of a Li–air battery with and without electrocatalysts [1–3], furthermore using carbon by itself has shown to provide high catalytic activity [4–6]. However, most of these studies were performed with organic electrolytes based on carbonates which undergo decomposition and form stable products such as  $\text{Li}_2\text{CO}_3$  instead of the desired products (i.e.,  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$ ) [7,8]. This decomposition contributes to the overpotential of the discharge/charge mechanism, interfering with the validation of new electrocatalyst. There is still a need to find a suitable electrolyte that can be stable during the harsh and oxidizing conditions

found in this battery. More recently, ethers such as 1,2-dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME) had been considered as stable solvents during oxidative conditions and selectively promote the formation of  $\text{Li}_2\text{O}_2$  during ORR [9–11].

The inherent complexity of the Li/air battery makes it very difficult to predict and understand catalyst behavior in the cathode. Also, different carbon morphologies can have an effect in performance. For this study, Lithium bis(trifluoromethylsulfonyl)imide ( $\text{LiTF}_2\text{N}$ ) in TEGDME was used as the electrolyte for comparing the performance of different air electrode materials. TEGDME was selected as the solvent as it has been demonstrated to have high solubility for  $\text{LiTF}_2\text{N}$  and a wide electrochemical window [12]. The different carbon materials were tested for ORR and OER performance using cyclic voltammetry (CV) in a three electrode setup. The experiments seek to evaluate the potentials and reversibility of the reactions occurring at the surface of the air electrode materials without the variables that can affect the performance during full cell assembly testing.

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## 2. Experimental

The materials used were commercially acquired and listed in Table 1. The surface area was obtained utilizing a Micromeritics ASAP2020C, with a 17-point  $N_2$  adsorption–desorption isotherm at 77 K. The  $LiTF_2N$  and TEGDME were purchased from 3 M and from Sigma–Aldrich, respectively. Molecular sieves were placed inside the electrolyte solution 24 h prior to use to reduce moisture content. Handling of the electrolyte solution was done inside an Ar filled glovebox. Electrolyte solutions were used when the water content of <100 ppm was achieved. A Karl Fisher Titration was used to determine the moisture content.

Performance for the ORR and OER was obtained using a BASI RDE-2 rotator system enclosed by a plastic glovebox with a continuous flow of dry argon. The system was connected to a computer controlled BASI potentiostat with Epsilon software. The electrodes used consisted of a platinum coil as the counter electrode, a 3 mm diameter disk made of carbon glassy (CG), or gold as the working electrode, and an E-DAQ reversible hydrogen electrode as the reference electrode. The reference potential in the electrolyte solution was 2.72 vs.  $Li/Li^+$  as measure from a Li strip in a solution of 1 M  $LiTF_2N$  in TEGDME. Cyclic voltammetry experiments ran between 1.15 and 3.92 V vs.  $Li/Li^+$  for 10 cycles first in a  $N_2$  bubbled solution and then in an  $O_2$  bubbled solution at a scan rate of  $100\text{ mV s}^{-1}$ . The data from the  $N_2$  bubbled solution was used to correct for the background current for the performance of during cycling in the  $O_2$  bubbled solution. Carbon inks were prepared with 8 mg of the carbon dispersed in 4 mL of deionized (DI) water and 4 mL of ethanol. For the carbon and manganese containing inks, 4 mg of carbon and 4 mg of QuantumSphere<sup>®</sup> manganese/manganese oxide were dispersed in 4 mL of DI water and 4 mL of ethanol. A volume of  $3.5\ \mu\text{L}$  was placed on top of the working electrode. After it dried at room temperature,  $2\ \mu\text{L}$  of a solution of 0.2% w/w of Nafion<sup>®</sup> in Ethanol was added as a binder. All of the experiments were run at room temperature. The voltammograms presented in Figs. 1 and 2 correspond to a section of the CV. For ORR (Figs. 1(a) and 2(a)) the cathodic scan from 3.5 V to 1.15 V is displayed and for OER (Figs. 1(b) and 2(b)) the anodic scan from 3.5 V to 3.92 V is displayed.

## 3. Results and discussion

ORR and OER performance of the electrode itself (without the addition of the carbon inks) in 1 M  $LiTF_2N/TEGDME$  was first determined by testing electrodes of CG and Au. The potential window during CV was maintained during all experiments to maintain similar peak behavior during OER. It was observed that for OER the shape of the peak can change depending on the selection of a reduction potential limit because as the potential shifts negatively a broad peak can develop in the OER area indicating more than one reduction reaction [10]. Fig. 1 presents the voltammograms of ORR (a) and OER (b) performance while oxygen was being flown in the

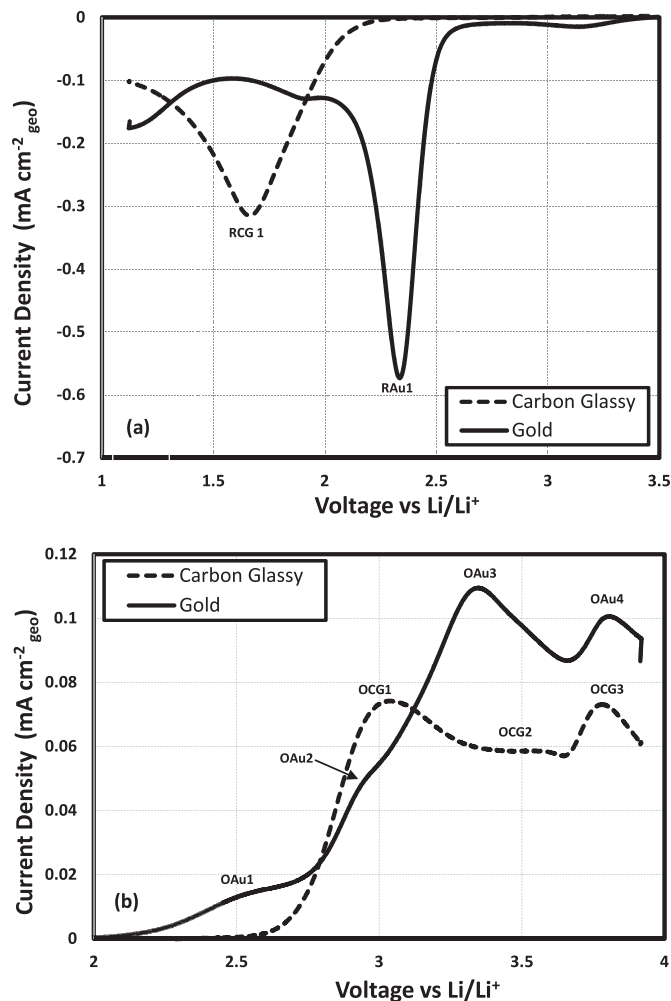


Fig. 1. (a) ORR and (b) OER curves of Carbon Glassy (CG) and Gold (Au) electrode at room temperature.

cell. For ORR a main peak is observed corresponding to reduction peak of CG (RCG1) and reduction peak of Au (RAu1). Compared to CG, Au electrode starts at a lower potential (2.6 V) than CG (2.3 V) for ORR. Additionally the current density is  $0.573\text{ mA cm}^{-2}_{\text{geo}}$  which is about 45% higher than CG. Therefore, as observed by other researchers Au is more active than CG for ORR [13]. During the oxidation scan, where OER occurs, Au starts at a lower potential than CG, however several oxidation peaks are observed (OAu1, OAu2, OAu3 and OAu4). In the case of CG two main peaks and a broad peak are observed (OCG1, OCG2 and OCG3). These peaks also have less current density than ORR due to insoluble reduction products that can adsorb on the surface of the disk blocking reaction sites. For accounting of the OER, the voltage at  $\sim 3.5\text{ V}$  in

Table 1  
Physical properties of the different materials tested.

Carbon material	BET surface area ( $\text{m}^2\text{ g}^{-1}$ )	Pore volume ( $\text{cm}^3\text{ g}^{-1}$ )	Particle size <sup>b</sup>
Carbon black (Vulcan XC-72R, Cabot, Inc.)	220	0.35	$27\text{ nm}^a$
Carbon black (Ketjenblack EC600JD, Akzo Nobel)	1410	2.72	$4\text{ nm}^a$
Carbon nanofiber (PR-19-XT-HHT, Pyrograf III)	8	0.05	$150\text{ nm} * 50\text{--}200\ \mu\text{m}$
Single-wall carbon nanotubes (Bucky USA)	1115	0.98	$0.7\text{--}2.5\text{ nm} * 0.5\text{--}10\ \mu\text{m}$
Multi-wall carbon nanotubes (Sigma–Aldrich)	299	0.88	$20\text{--}25\text{ nm} * 1\text{--}5\ \mu\text{m}$
Manganese/manganese oxide QSI-Nano <sup>®</sup> (QuantumSphere)	26	0.14	$30\text{--}50\text{ nm}$

<sup>a</sup> As determined by BET.

<sup>b</sup> Particle size as reported by manufacturer unless otherwise noted.

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