



## Short communication

## Investigation of the electrocatalytic oxygen reduction and evolution reactions in lithium–oxygen batteries

Dong Zheng <sup>a</sup>, Xuran Zhang <sup>b</sup>, Deyu Qu <sup>b</sup>, Xiao-Qing Yang <sup>c</sup>, Hung-Sui Lee <sup>c</sup>, Deyang Qu <sup>a,\*</sup><sup>a</sup> Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin Milwaukee, Milwaukee, WI 53211, USA<sup>b</sup> Department of Chemistry, School of Science, Wuhan University of Technology, Wuhan, 430070 Hubei, PR China<sup>c</sup> Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

## H I G H L I G H T S

- Over-potential for the redox reaction  $O_2/O_2^{\cdot-}$  is low, no catalyst is needed.
- Carbon edge plane shows the same catalytic activity as the basal plane for ORR.
- Strong Lewis acid assists solid  $Li_2O_2$  becoming soluble.
- The soluble  $B - O_2^{\cdot-}$  can be electrochemically oxidized.
- Carbon edge plane shows superior catalytic activity for the oxidation of  $B - O_2^{\cdot-}$ .

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## A B S T R A C T

Oxygen reduction and oxygen evolution reactions were studied on graphite electrodes with different crystal orientations. The kinetics for the redox couple  $O_2/O_2^{\cdot-}$  are very fast, therefore no catalyst seems necessary to assist the charge transfer process. Apparently, the main source of the overpotential for the  $O_2$  reduction reaction is from mass diffusion.  $Li_2O_2$  becomes soluble in non-aqueous electrolytes in the presence of the tetraethylammonium tetrafluoroborate additive. The soluble  $B - O_2^{\cdot-}$  ions can be oxidized electro-catalytically. The edge orientation of graphite demonstrates superior catalytic activity for the oxidation over basal orientation. The findings reveal an opportunity for recharging Li-air batteries efficiently and a new strategy of developing the catalyst for oxygen evolution reaction.

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## 1. Introduction

Owing to the promising energy density relative to state-of-art Li-ion batteries, Li-air batteries have been extensively investigated recently. The energy efficiency, which depends mainly on the kinetics of the redox reaction, i.e. the electrochemical over-potential of the  $O_2$  reduction reaction (ORR) and the  $O_2$  evolution reaction (OER), remains low. The current research aims to investigate the electrocatalytic ORR and OER reactions.

In the past few years, most of the research on Li-air chemistry was focused on catalysts on the positive electrode aiming to enhance the ORR rate and the rate for re-oxidation of  $Li_2O_2$

precipitates. Several candidates were studied including metal oxides (e.g.  $MnO_2$ ,  $CuO$  and  $Fe_3O_4$ ) and noble materials (e.g. Pt, Au) [1–3]. Electrochemical adsorption of oxygen molecules on the surface of the catalyst is believed to be the first step in the catalytic  $O_2$  reduction [4]. Such adsorption must be strong enough to at least facilitate charge transfer and/or to weaken the O–O bond enabling the 4-electron reduction reaction. A good example is the electrocatalytic ORR in aqueous electrolyte by  $MnO_2$  catalyst (2-electron reduction) and Pt catalyst (4-electron reduction). Thus,  $O_2$  and the electrolyte have to first migrate to the interface and establish an intimate physical contact with catalyst particles on the electrode. The process is essential for the electrocatalytic reaction to occur. Indeed, higher electrocatalysis for the ORR on the surface with increasing binding energy of  $O_2$  has been reported [5]. However, with  $Li_2O_2$  building up on the surface of the electrode during discharge, mass transfer is hindered and the active sites on the

\* Corresponding author.

E-mail address: [qud@uwm.edu](mailto:qud@uwm.edu) (D. Qu).

electrode are covered, as well. Ideal electrocatalysis is likely not possible for non-aqueous Li-air discharge and charge since the reactant transport to and the product transport away from the catalyst are prohibited. The problem can only be alleviated if the path for mass transfer can be maintained [6]. To make things more complicated, after careful measurements of the reaction products, the previously reported effective OER catalysis of  $\text{Li}_2\text{O}_2$  was actually the electrocatalysis of electrolyte solvent decomposition. No catalysts were found to be effective including  $\text{MnO}_2$ , Pt, and other nanocatalysts for the OER in the oxidation process of  $\text{Li}_2\text{O}_2$ ; non-aqueous electrolyte solvent decomposition on the electrode was the dominant reaction [7]. In this research, ORR and OER on graphite electrodes with various crystal orientations were investigated in order to understand the impact of different catalytic surface.

## 2. Experimental details

The electrochemical measurements were conducted in a 4-neck, jacketed glass cell. The working electrode was a rotating disk electrode (RDE) that consisted of a disc 5.0 mm in diameter (Pine Research Instrumentation). Pt, glassy carbon, edge orientation graphite and basal orientation graphite disk electrodes were used. The RDE assemblies were polished using rayon cloth with 0.05  $\mu\text{m}$  alumina slurries and ultrasonically cleaned. The cells were assembled in an Ar-filled glove box before being transferred to a dry air-filled glove box where the experiments were conducted. The Pt wire and all-solid Ag/AgCl electrode were used as counter electrode and reference electrode. The cells were purged with dry  $\text{O}_2$  for half an hour before the  $\text{O}_2$  reduction experiment was performed by CBP Bipotentiostat system (Pine Research Instrumentation) with AfterMath software (version 1.2.4361).

## 3. Results and discussion

In a Li-air battery, a carbon gas diffusion electrode (GDE) is always used as the cathode and the catalysts are loaded into the matrix of the porous carbon. Similar GDEs are used in Zn-air batteries and fuel cells with aqueous electrolytes. The electrocatalytic ORR on the carbon surface in aqueous electrolyte has been investigated in detail. It was reported that the catalysis for the ORR is significantly different on the basal and edge orientations of graphite, where the edge orientation demonstrated substantially higher electrocatalytic activity for the ORR [8]. The specific catalytic activity of the high surface area carbon used to make the GDE was determined by the percentage of the edge orientation of the surface [8]. Fig. 1 shows the cyclic voltammetry of the ORR on the carbon surface with different orientations. It has been well reported that non-aqueous electrolytes can react with  $\text{O}_2^{2-}$ . To alleviate the issue of electrolyte stability during the reduction of  $\text{O}_2$ , acetonitrile, which has proven to be stable during the redox reaction of  $\text{O}_2$  was chosen as the solvent. Tetraethylammonium tetrafluoroborate ( $\text{TEABF}_4$ ) was used as the electrolyte. Any electrolyte decomposition, especially those associated with charge transfer, can be ignored [9], therefore we only investigated the electrocatalysis of the  $\text{O}_2$  redox reaction.

Unlike in aqueous electrolyte, no difference can be observed for the electrocatalytic activity for the ORR on the various carbon surfaces. One can easily observe the differences between the cyclic voltammetry for the ORR in alkaline electrolyte (Fig. 2 in ref. 8) and that in non-aqueous electrolyte shown in Fig. 1. Besides the clear difference in the electrocatalytic activity on various carbon orientations, the  $\text{O}_2$  redox reaction was very irreversible in the alkaline electrolyte, but very reversible in acetonitrile-based electrolyte. Hence, the activation energy or the over-potential for the ORR and OER in acetonitrile would be considerably lower. Since a catalyst

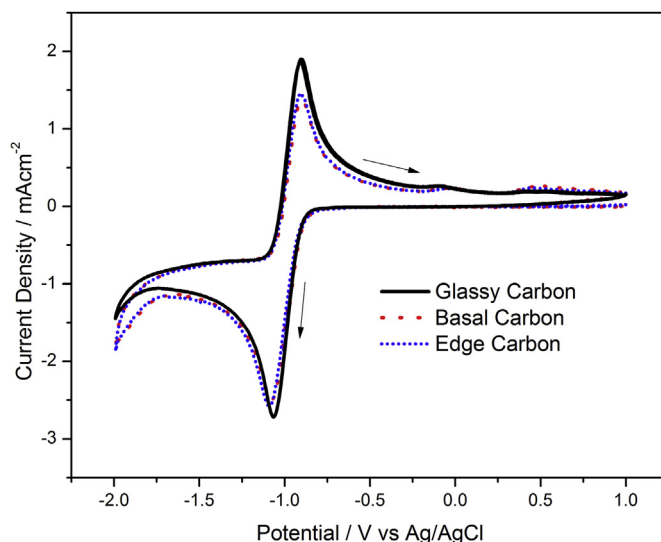


Fig. 1. Cyclic voltammetry for the  $\text{O}_2$  redox reaction on the surface of pyrolytic graphite (PG) edge layer, PG basal layer and glassy carbon in 0.1 M  $\text{TEABF}_4$  acetonitrile electrolyte saturated with  $\text{O}_2$ . The scan rate is 50 mv/s.

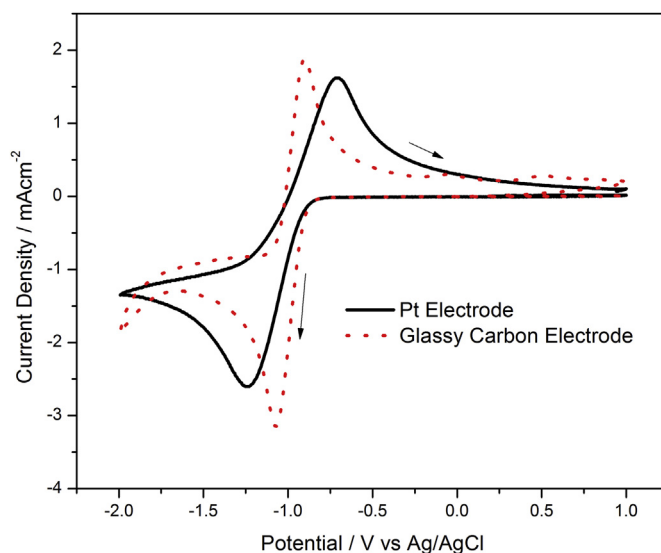


Fig. 2. Comparison of cyclic voltammetry of  $\text{O}_2$  redox reaction on glass carbon and Pt electrodes in 0.1 M  $\text{TEABF}_4$  acetonitrile electrolyte saturated with  $\text{O}_2$ . The scan rate is 50 mv/s.

increases the rate of a reaction by reducing the activation energy, with an already low activation energy, the catalyst would have minimal impact on the kinetics of the  $\text{O}_2$  redox reaction in acetonitrile. In addition, the possible absorption of organic molecules on the graphite electrodes could also level the electrochemical catalytic capability. It seems that all of the electron transfer processes are faster in acetonitrile and therefore the reactions would be limited by the mass transport rate. It is worth pointing out that the 2-e ORR occurs in alkaline electrolyte but the ORR in non-aqueous electrolyte is the 1-e reaction. The products of the reduction are  $\text{O}_2^{2-}$  and  $\text{O}_2^{\cdot-}$ , respectively. The  $\text{O}_2^{\cdot-}$  can survive for substantial length of time with the lack of Lewis acid.

Fig. 2 shows the comparison of the cyclic voltammetry for the ORR and OER on Pt electrode and glassy carbon electrode. Interestingly, the redox reaction on the carbon surface was much more

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