Mechanism of Oxygen Reduction in Aprotic Li–Air Batteries: The Role of Carbon Electrode Surface Structure

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Supporting Information

ABSTRACT: Electrochemical oxygen reduction in aprotic media is a key process that determines the operation of advanced metal–oxygen power sources, e.g., Li–O2 batteries. In such systems oxygen reduction on carbon-based positive electrodes proceeds through a complicated mechanism that comprises several chemical and electrochemical steps involving either dissolved or adsorbed species, and as well side reactions with carbon itself. Here, cyclic voltammetry was used to reveal the effects of imperfections in the planar sp² surface structure of carbon on the Li oxygen reduction reaction (Li-ORR) mechanism by means of different model carbon electrodes (highly oriented pyrolytic graphite (HOPG), glassy carbon, basal, and edge planes of pyrolytic graphite), in dimethyl sulfoxide (DMSO)-based electrolyte. We show that the first electron transfer step \( \text{O}_2 + e^- \rightarrow \text{O}_2^- \) (followed by ion-coupling \( \text{Li}^+ + \text{O}_2^- \rightarrow \text{LiO}_2 \)) does not involve oxygen chemisorption on carbon as evidenced by the independence of its rate on the carbon electrode surface morphology. The second electron transfer leading to \( \text{Li}_2\text{O}_2 \) (\( \text{Li}^+ + \text{LiO}_2 + e^- \rightarrow \text{Li}_2\text{O}_2 \)) is strongly affected by the electrode surface even in highly solvating DMSO. Formation of \( \text{Li}_2\text{O}_2 \) via the electrochemical reaction could be observed only on the nearly ideal basal plane of graphite. In contrast, for more disordered electrode surfaces, (and/or bulk) the only reduction peak revealed on cyclic voltammograms corresponds to \( \text{LiO}_2 \) formation, supporting that solution-mediated mechanism for \( \text{Li}_2\text{O}_2 \) growth is more favorable in that case. We also show that increased defect concentrations on the carbon electrode surface promote the formation of \( \text{Li}_2\text{CO}_3 \) during ORR, albeit relatively slower than \( \text{Li}_2\text{O}_2 \) formation.

INTRODUCTION

Electrochemical oxygen reduction and evolution reactions (ORR and OER) have been of great interest for decades. This mainly arises from the advantages of using oxygen-based redox couples for energy storage and conversion. The low molecular weight and high oxidative ability of oxygen provide potentially significant improvements to the key characteristics of batteries and fuel cells, namely, working voltage and specific capacity.¹

According to some estimates the Li–O₂ battery with aprotic electrolytes can enable specific energies up to 0.7–1 kWh/kg.₂ Unlike fuel cell cathodes that contain ORR catalysts (mainly noble metals) providing direct 4-electron oxygen reduction to water, in Li–O₂ batteries with nonaqueous electrolytes, 2-electron reduction to main discharge product, Li₂O₂, readily occurs on plain carbon electrodes. However, despite the achievement of high capacities (up to 16 Ah/g with some nanostructured carbon electrodes)³, low discharge current densities and poor cyclability limits Li–O₂ battery operation to several cycles only.⁴ The reason primarily lies in slow ORR/OER kinetics and complex multistep reaction pathways. The reaction mechanism of Li-ORR on carbon electrodes has been a matter of some dispute for years, and various elementary steps that have been proposed are given in Table 1. Koutecky–Levich analysis provides an evidence that the rate-determining step of Li-ORR is one-electron reduction of oxygen.⁵,⁶ In contrast to TBA⁺-containing aprotic electrolytes, where ORR proceeds according to reaction I in Table 1, the presence of Li⁺ ions results in a substantial positive shift of the ORR potential, indicating the formation of solvated lithium superoxide intermediate LiO₂ (reactions Ia, Ib).⁵,⁷ Some authors⁸ suggest that reaction Ib is actually composed of two time-separated steps, I and Ia, occurring in solution. Although solid-state LiO₂ can be obtained below 25 K only,⁹ the existence of superoxide species on the surface of discharged electrodes was revealed by Raman spectroscopy,¹⁰¹¹¹² X-ray diffraction (XRD),¹³ X-ray absorption near edge structure (XANES),¹⁴ and operando X-ray photoelectron spectroscopy.
Table 1. Summary of Experimental Studies of Li-ORR Elementary Steps on Carbon Electrodes

<table>
<thead>
<tr>
<th>N</th>
<th>discharge steps</th>
<th>electrode</th>
<th>electrolyte</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>O₂ + e⁻ ⇌ O₂⁻</td>
<td>activated carbon</td>
<td>TEGDME/Li triflate</td>
<td>9</td>
</tr>
<tr>
<td>Ia</td>
<td>O₂⁻ + Li⁺ ⇌ LiO₂</td>
<td>GC</td>
<td>DMSO/LiPF₆</td>
<td>6</td>
</tr>
<tr>
<td>Ib</td>
<td>Li⁺ + O₂ + e⁻ ⇌ LiO₂</td>
<td>activated carbon</td>
<td>DMSO/LiPF₆</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>(carbon black, GC)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GC</td>
<td>MeCN/LiPF₆</td>
<td>5</td>
</tr>
<tr>
<td>IIa</td>
<td>LiO₂ + Li⁺ + e⁻ ⇌ Li₂O₂</td>
<td>GC</td>
<td>TEGDME/Li triflate</td>
<td>22</td>
</tr>
<tr>
<td>Iib</td>
<td>2LiO₂ ⇌ Li₂O₂ + O₂</td>
<td>(sol)</td>
<td>TEGDME/LiTFSI</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GC</td>
<td>PyRFTFSI/LiTFSI</td>
<td>27</td>
</tr>
<tr>
<td>IIC</td>
<td>2LiO₂ ⇌ Li₂O₂ + O₂</td>
<td>(sur)</td>
<td>TEGDME/LiTFSI</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>GC</td>
<td>TEGDME/LiPF₆</td>
<td>9</td>
</tr>
<tr>
<td>IIIa</td>
<td>LiO₂ + 2Li⁺ + 2e⁻ ⇌ 2Li₂O</td>
<td>carbon black, GC</td>
<td>DMSO/LiPF₆</td>
<td>25</td>
</tr>
<tr>
<td>IIIb</td>
<td>LiO₂ + 2Li⁺ + 2O₂</td>
<td>GC</td>
<td>DMSO/LiPF₆</td>
<td>6</td>
</tr>
<tr>
<td>IV</td>
<td>LiO₂ + C ⇌ Li₂CO₃</td>
<td>RGO</td>
<td>LATP</td>
<td>14</td>
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<tr>
<td></td>
<td>carbon black</td>
<td>DME/LiTFSI</td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>


(XPS) analysis, as well as magnetic measurements. The possibility of electrochemical reduction (reaction IIa) of solvated LiO₂ was suggested in a number of works and supported by density functional theory (DFT) calculations. This pathway was later proposed to become dominant at high reduction overpotentials. Disproportionation of solvated LiO₂ (reaction IIB) is an alternative pathway that has been shown to occur in the electrolyte using chemical experiments where Li₂O₂ precipitates from lithium salt solutions after KO₂ addition. This pathway prevails at low overpotentials and strongly depends on the solvent’s nature. Recent works report that decreasing Li⁺ and O₂⁻ combined solvation (determined by the solvent’s donor and acceptor number, respectively) lowers the stability of the LiO₂ ionic pair, thus promoting LiO₂ via disproportionation. Surface-mediated disproportionation of LiO₂ species (reaction IIC) on carbon electrodes was reported as well. Some evidence of Li₂O formation due to electrochemical reaction at high overpotentials (reaction IIIa) or chemical processes (reaction IIIb) were presented.

Besides the above-mentioned processes, carbon could also be involved in Li₂CO₃ formation due to its interaction with LiO₂. CO₂ evolution during battery charge was detected by differential electrochemical mass spectrometry (DEMS) and provided evidence for the electrochemical decomposition of the Li₂CO₃ byproduct.

Another important issue that affects Li-ORR mechanism is the chemical reactivity of solvents with Li₂O₂ and LiO₂ intermediate. A number of experimental studies and theoretical predictions focused on the solvent reactivity with superoxide species and LiO₂ demonstrated that most solvents react chemically with Li₂O₂ discharge products.

Although surface-mediated reactions play an important role in the Li-ORR mechanism, especially at high reduction overpotentials, much less attention is paid to the influence of electrode surface structure on Li-ORR mechanism. Carbon materials have quite complex surface chemistry due to diversity of bond types and functional groups, which can affect wetting, adsorption, electron transfer kinetics, electrocatalysis, etc.

A large number of works have suggested that the basal surface of graphene is characterized by rather poor electrode kinetics, compared to edge plane, for a wide range of redox couples, including classical outer- and inner-sphere. The current densities for the reduction of O₂ to O₂⁻ and HO₂⁻ are far lower on the basal plane of graphite that for O₂ reduction on pyrolytic graphite and glassy carbon in alkaline solutions. This implies that O₂ reduction on carbon and graphite involves strong interaction of O₂ with functional groups on the surface. Some evidence of the role of carbon electrode structure on discharge reactions in Li₂O₂ electrochemistry was also found. DFT calculations showed that functional groups and defects in graphite sp² lattice affect O₂ and LiO₂ adsorption. By evaluating the discharge performance of Li₂O₂ batteries with cathodes based on oxidized carbon nanotubes with various oxygen content, the catalytic effect of oxygen functionalities in Li-ORR was examined. The active edges of the graphene layers at carbon surface were reported to be indispensable for controlling the morphology of Li₂O₂ deposits and improving battery performance. The important role of carbon defects in carbon’s reactivity toward superoxide species was also highlighted.

However, experimental mechanistic studies of Li-ORR have been performed in various cell types, employing carbon materials (glassy carbon, porous activated carbon and carbon black), which possess different porosity, wettability and thus electrochemically active surface area, often using polymer binders. All this hinders correct determination of carbon surface structure effect on oxygen reduction pathways.

Here, we systematically investigate the impact of carbon defects on Li-ORR mechanisms by probing it in several model systems. We employed cyclic voltammetry on carbon disk electrodes with controllable surface structure: highly oriented pyrolytic graphite (HOPG), basal and edge plane of pyrolytic graphite (PG-basal and PG-edge, respectively), and conventional glassy carbon (GC). Dimethyl sulfoxide (DMSO), despite its reported reactivity with Li₂O₂ upon prolonged exposure, was chosen as an electrolyte solvent due to its reasonable short-term stability in the presence of superoxide intermediates, and higher LiO₂ disproportionation stability, which allows us to trace the disproportionation reactions on the electrode surface. Using HOPG electrode enabled separation of two electrochemical reduction peaks, which we attributed to O₂ + e⁻ ⇌ O₂⁻ and LiO₂ + e⁻ + Li⁺ ⇌ Li₂O₂. The cyclic voltammetry results show that disordered GC surface prevents further electrochemical reduction or disproportionation of LiO₂ species, in contrast to HOPG, while at the same time promoting much slower reaction with Li₂O₂ resulting in the
formation of lithium carbonate. LiO₂ disproportionation in solution is thus the major process that governs the Li₂O₂ formation in DMSO-based electrolyte on carbon electrodes with high amount of defects, even at high reduction overpotentials.

**EXPERIMENTAL SECTION**

The glassy carbon and all pyrolytic graphite disk electrodes (all 3 mm in diameter) were purchased from ALS Co., Ltd. HOPG disk electrode was fabricated in-house by cutting the 3 mm diameter cylinder from the HOPG crystal parallel to its basal plane and sealing it in a polyetheretherketone (PEEK) tube with an integrated stainless steel rod providing electric contact. For XPS analysis, glassy carbon piece and HOPG crystal were used as electrodes. Glassy carbon and pyrolytic graphite electrodes were polished with 1 μm and 50 nm alumina and ultrasonicated in ethanol prior to experiments. The clean surface of HOPG electrodes was obtained by cleaving the top layer with a sticky tape.

An airtight three-electrode electrochemical cell was designed and built in-house and consisted of Ag+/Ag reference electrode (Ag wire in a solution of 0.01 M AgNO₃ and 0.1 M TBAClO₄ in anhydrous acetonitrile (all reactants purchased from Sigma-Aldrich)) and platinum wire counter electrode. The Ag+/Ag electrode potential was determined by calibration versus the ferrocenium/ferrocene (Fc+/Fc) redox couple (0.02 M solution of ferrocene (98%, Sigma-Aldrich) in DMSO-based electrolyte was used). The potentials are represented versus standard Li⁺/Li (−3.05 V vs SHE). Solutions of lithium perchlorate (LiClO₄, battery grade, Sigma-Aldrich) and/or tetrabutylammonium perchlorate (TBAClO₄ for electrochemical analysis, Sigma-Aldrich) in DMSO (Acros chemical company) were used as electrolytes. Water content in the electrolyte solutions was estimated to be less than 30 ppm before, and less than 100 ppm after the measurements, as determined by Karl Fischer titration. The volume of electrolyte used for each experiment was ca. 3 mL. The electrochemical cells were assembled in an Ar-filled glovebox (Labconco) where H₂O and O₂ concentrations were kept below 5 and 30 ppm, respectively.

High-purity oxygen was purged through the cell using gas inlet while gas outlet was connected to environment via hydroseal with silicone oil. The electrochemical measurements were performed with a BioLogic SAS SP-300 potentiostat/galvanostat. The electrodes were cycled continuously in potentiodynamic mode (potential sweep rate 100 mV/s) with a certain density of domain boundaries (mean domain size is about 100 nm). Another PG electrode primarily exposes graphene layer edges to the electrolyte solution. GC electrode is about 100 nm). Another PG electrode primarily exposes graphene layer edges to the electrolyte solution. GC electrode (Figure 2a). HOPG presents a nearly ideally ordered surface with an sp²-hybridized carbon atom network. The PG basal surface demonstrates a disorder in lateral crystallite orientation with a certain density of domain boundaries (mean domain size is about 100 nm). Another PG electrode primarily exposes graphene layer edges to the electrolyte solution. GC electrode is a combination of the sp² fragments on sp³ matrix both in bulk and at the surface.

Raman spectroscopy was used to characterize the carbon crystallinity. The Raman spectrum of HOPG electrode consists of two dominant features: G-band (1580 cm⁻¹) associated with the longitudinal optical (LO) phonon mode, and second-order dispersive 2D-band (2670 cm⁻¹). D-band feature (1370 cm⁻¹) appears in disordered carbons due to the presence of edges, stacking disorder between two layers, and atomic defects within the layer. The disorder-induced D’-band (1630 cm⁻¹) is responsible for intravalley double resonance Raman process. The ratio between D- and G-band integral intensities (Figure 2a).

**RESULTS AND DISCUSSION**

The role of carbon electrode surface structure in Li-ORR mechanisms was studied by means of cyclic voltammetry in oxygen-saturated 0.1 M LiClO₄ in DMSO. Carbon electrodes that were chosen for the analysis have different morphologies (Figure 1) and amount of defects according to Raman spectra.
2a) is normally used to evaluate the structural disorder of carbon materials.

Typical cyclic voltammograms of carbon electrodes at a sweep rate of 100 mV/s are shown in Figure 2b. In contrast to GC and PG-edge electrodes, HOPG and PG-basal electrodes, which have comparable surface, were found to show two well-resolved reduction peaks (c1 and c2 in Figure 2b). Peak c1 at ca. 2.5 V was always observed on glassy carbon electrodes, in either Li+- or TBA+-containing electrolytes and has been attributed previously to the reaction Li+ + O2 + e− ⇌ LiO2 or TBA+ + O2 + e− ⇌ TBAO2.5

Peak c2 at ca. 2 V has never been observed previously on carbon electrodes in Li+-containing electrolytes; however, it was detected in cyclic voltammograms of Au electrodes18 in Li+-containing electrolytes. It was assigned to the reactions LiO2 + Li+ + e− ⇌ Li2O2 or TBAO2 + TBA+ + e− ⇌ TBA2O2, respectively.

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At the same time, c2 peak current depends on Li+ concentration (Figure 3a), and linearly scales with it in the range of 1--6 mM (Figure 3a, inset) supporting the first-order reaction with respect to Li+ ions and indicating that LiO2 associates were previously formed in the solution:

\[ \text{LiO}_2 + \text{Li}^+ + e^- \xrightarrow{} \text{Li}_2\text{O}_2 \]

The reaction c2 is likely to involve LiO2 species adsorbed on electrode surface, as it is sensitive to the electrode passivation. Successive lowering of the anodic limit while recording cyclic voltammograms increases the amount of solid product left on the surface on the following cycle, which results in substantial decrease of the c2 peak current (Figure 3b). At the same time, c1 peak current is insensitive to electrode passivation, which may indicate that reaction c1 does not involve preliminary oxygen adsorption (Figure 3b).

The anodic semicycle is very informative and reveals the decomposition of discharge products that have been generated on the electrode surface. On GC electrodes it includes several peaks that were attributed in different works to oxidation of LiO2 (3.5 V44, 2.6 V23), Li2O2 (3.75 V44, 3.6 V9, 3.2 V23) LiO2− (3.2 V9), Li3CO3 (4.5 V25, 4.2 V24) and Li2O (4.2 V9, 3.8 V25). Previously reported galvanostatic charging experiments demonstrated that two charge plateaus on activated carbon electrodes at the potentials of 3.2 and 4 V22 can be assigned to Li2O and LiO2 oxidation, respectively. A small anodic peak below 2 V could be connected with the oxidation of (TBA)2O2 to (TBA)O2; however, further studies are required in order to prove it.

To investigate the nature of the anodic peaks on HOPG and GC surfaces, we performed potentiostatic holding at c1 and c2 peak potentials, which was followed by linear anodic sweep voltammetry (Figure 4). After potentiostatic holding at 2.4 V (c1 peak potential for GC) and 2.0 V, the GC electrode was...
found to exhibit a single well-resolved anodic peak a1 at 3.2 V in both cases (Figure 4c,d). The HOPG electrode was held at 2.2 and 1.9 V (c1 and c2 peak potentials for HOPG, respectively), and in contrast to GC the potentiostatic hold at c2 peak potential gave rise to the additional anodic peak a2 at ca. 4 V (Figure 4a,b).

Taking into account reduction reactions that correspond to the c1 and c2 peaks according to our data and to the literature,44 we propose the following scheme for the anodic process. We ascribe the peak a1 to adsorbed LiO2 oxidation:

\[
\text{LiO}_2(\text{ads}) \rightleftharpoons \text{Li}^+ + \text{O}_2 + e^- 
\]

and peak a2 to oxidation of Li2O2:

\[
\text{Li}_2\text{O}_2(\text{ads}) \rightleftharpoons 2\text{Li}^+ + \text{O}_2 + 2e^- 
\]

The peak a2 is very weak on GC electrode, in contrast to HOPG surface, that may indicate that the surface-bound Li2O2 cannot be formed on defective GC electrode. On HOPG the a2 peak current increases when potentiostatic hold is carried out at lower potential (c2) enabling electrochemical LiO2 reduction. We can assume that LiO2 is stabilized by carbon surface defects preventing both surface-mediated disproportionation and further reduction to Li2O2. This result is in agreement with previous work,37 suggesting that the structure of activated carbon electrode provides a suitable environment for surface stabilization of lithium superoxide compound. Although these species were reported to be prone to disproportionation to Li2O2,12 it was shown by X-ray diffraction and Raman spectroscopy that LiO2 can survive for several days9 by being stabilized by carbon surface.12 DFT calculations suggested that oxygen-containing defects on the carbon surface might be responsible for such stabilization.37

One more anodic peak a3, whose origin is questionable, is observed on both HOPG and GC at the potential 4.4–4.6 V (see Figure 4). This peak can be ascribed to the decomposition of byproducts generated in side-reactions with superoxide species. The anodic peak at the potentials 4.2–4.5 V was previously reported for GC electrode in dimethoxyethane (DME)-based electrolyte and was attributed to the Li2CO3 decomposition, as it was accompanied by CO2 evolution according to DEMS measurements.44 This peak also appears on anodic voltammetric sweeps after treatment of glassy carbon electrodes with KO2 powder in Ar atmosphere.14 In other works utilizing DMSO- and DME-based electrolytes, the anodic peak in the same region was ascribed to Li2O6 or LiOH decomposition,45 as well as to the products of electrolyte side reactions.45 Pt electrode, however, shows no peaks in the potential region >4 V in the same electrolyte solvent (see Figure S2). Taking into account that a3 peak current increases with potential holding time (Figure 4) for both GC and HOPG, it likely arises from oxidation of the species produced by reaction of carbon electrode with superoxide, e.g., Li2CO3.

We performed ex situ NEXAFS and XPS analysis of HOPG and GC electrodes recovered from Li/O2 electrochemical cells after potentiostatic holding at c1 peak potentials in O2-saturated 0.1 M solution of LiClO4 in DMSO. The depth of discharge was equal to 0.3 μAh/cm2 (equivalent to the charge required to produce 16 monolayers of Li2O2 on electrode surface). The appearance of a Li 1s signal and increasing of O 1s intensity provides evidence of lithium- and oxygen-containing species forming on the electrode surfaces (Figure

**Figure 4.** Anodic LSV curves at 100 mV/s in 0.1 M LiClO4 in DMSO, recorded after potentiostatic holds of different duration on HOPG electrode (a, b) and on GC electrode (c, d). Hold potentials are indicated by vertical dashed lines, while durations are indicated by different colors. Thin gray dashed lines show typical cyclic voltammograms for the corresponding electrodes at the same sweep rate.
Special efforts were taken to ensure that no electrolyte remained on the electrode: S 2p, Cl 2p and Li 1s spectra collected before and after soaking the electrode into the electrolyte were used for monitoring proper removal of the electrolyte residues (Figure S3). Small amounts of Li- and O-containing electrolyte components were detected on the surface after soaking, which could not account for the observed increases in Li and O signals after cathodic process.

Figure 5. NEXAFS C−K edge spectra of HOPG and GC electrodes before (blue) and after (pink) potentiostatic holding at 2.2 or 2.4 V, respectively. Discharge was performed in 0.1 M LiClO₄ in oxygen-saturated DMSO. The cell comprised Ag⁺/Ag reference electrode and Pt counter electrode. The cell was assembled and disassembled inside an Ar-filled glovebox. The HOPG and GC electrodes were transferred to the ultrahigh vacuum environment of the spectrometer under Ar atmosphere to avoid contact with ambient air.

Figure 6. C 1s photoemission spectra of HOPG (a, b) and GC (c, d) electrodes before (a, c) and after (b, d) potentiostatic holding at 2.2 or 2.4 V, respectively.
The NEXAFS C–K edge spectrum of pristine HOPG electrode (Figure 5a) demonstrates typical features for graphite lattice only: C 1s → π*(Cring) and C 1s → σ*(Cring) excitations at 285 and 291.5 eV, respectively. The spectrum of pristine GC surface (Figure 6b) additionally contains features corresponding to C 1s → σ*(C–H) excitation from aliphatic carbon atoms at 287 eV \(^{47}\) and C 1s → 1σ*(C=O) excitation from carboxyl groups at 288.5 eV \(^{47}\), which is expected for the highly defective structure of GC. After potentiostatic holding a sharp peak at 290.5 eV appears in spectra for both electrodes, having much higher intensity for GC. This feature was previously attributed to C 1s → π*(C=O) excitation of carbonate groups. \(^{47}\)

The quantitative estimations of relative \(\text{Li}_2\text{CO}_3\) amount were done using XPS analysis of the same electrodes. In contrast to HOPG, Li-ORR on GC electrode lead to noticeable increase of the components located at 290.6 eV and corresponding to carbon reactivity toward superoxide species in liquid DMSO-based electrolyte. \(^{14}\) Coupled with the hypothesis that more defective GC surface inhibits superoxide-to-peroxide conversion via disproportionation, these results allow us to assume that \(\text{Li}_2\text{O}_2\) is preferably captured by the defects and then could be involved in carbonate formation, which is a relatively slow reaction, rather than transforming to peroxide product.

Although we could not determine which type of defects (vacancies or domain boundaries, layer edges, decorated or not by oxygen-containing functionalities, etc.) are responsible for carbon electrode reactivity, defective carbon surfaces evidently have sufficiently high reactivity toward superoxide species in DMSO-based electrolyte. | ORR in a Li/O\(_2\) electrochemical system in DMSO-based electrolyte. It was found that the first electron transfer step from carbon electrode to oxygen molecule does not involve oxygen chemisorption and thus does not depend on electrode structure. By contrast, further electrochemical reduction to \(\text{Li}_2\text{O}_2\) could be observed only on the ideal basal plane of graphite and was found to be surface-mediated. Surface defects in GC stabilize \(\text{Li}_2\text{O}_2\) species on the surface, preventing them from surface-mediated disproportionation and further reduction to \(\text{Li}_2\text{O}_2\). Thus, the solution-mediated pathway should play the major role in \(\text{Li}_2\text{O}_2\) product formation. Both NEXAFS and XPS studies of discharged HOPG and GC electrodes data indicate the formation of \(\text{Li}_2\text{CO}_3\) as a byproduct and presumably carboxylic groups, which are more prominent on GC surface. This shows the role of carbon surface defects in carbon reactivity toward superoxide species in liquid DMSO-based electrolyte.

Table 2. Relative Contributions of Carboxyl and Carbonate Components in XPS Spectra of HOPG and GC Electrodes
<table>
<thead>
<tr>
<th>electrode</th>
<th>(I(\text{CO}_2^-),%)</th>
<th>(I(\text{COO}^-),%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG (basal)</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>glassy carbon</td>
<td>5.8</td>
<td>2.5</td>
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</table>

“Spectra were measured after potentiostatic holding at c1 peak potentials of HOPG and GC (2.2 or 2.4 V, respectively). The cathodic charge passed was 0.3 μAh/cm\(^2\) (equivalent to the charge required to produce 16 monolayers of \(\text{Li}_2\text{O}_2\) on electrode surface).” \(^{b}\)

Both NEXAFS and XPS data (Figures 5 and 6) indicate that the amount of \(\text{Li}_2\text{CO}_3\) and carboxylic functionalities formed during the discharge is much higher on the defective GC surface, in line with previously reported comparison of the stability of reduced graphite oxide and thermally exfoliated graphite electrodes toward superoxide species in all-solid-state cells. \(^{14}\) Coupled with the hypothesis that more defective GC surface inhibits superoxide-to-peroxide conversion via disproportionation, these results allow us to assume that \(\text{Li}_2\text{O}_2\) is preferably captured by the defects and then could be involved in carbonate formation, which is a relatively slow reaction, rather than transforming to peroxide product.

In conclusion, cyclic voltammetry technique was applied to trace the impact of carbon electrode surface structure on Li-ORR in a Li/O\(_2\) electrochemical system in DMSO-based electrolyte. It was found that the first electron transfer step from carbon electrode to oxygen molecule does not involve oxygen chemisorption and thus does not depend on electrode structure. By contrast, further electrochemical reduction to \(\text{Li}_2\text{O}_2\) could be observed only on the ideal basal plane of graphite and was found to be surface-mediated. Surface defects in GC stabilize \(\text{Li}_2\text{O}_2\) species on the surface, preventing them from surface-mediated disproportionation and further reduction to \(\text{Li}_2\text{O}_2\). Thus, the solution-mediated pathway should play the major role in \(\text{Li}_2\text{O}_2\) product formation. Both NEXAFS and XPS studies of discharged HOPG and GC electrodes data indicate the formation of \(\text{Li}_2\text{CO}_3\) as a byproduct and presumably carboxylic groups, which are more prominent on GC surface. This shows the role of carbon surface defects in carbon reactivity toward superoxide species in liquid DMSO-based electrolyte.

### CONCLUSIONS

In conclusion, cyclic voltammetry technique was applied to trace the impact of carbon electrode surface structure on Li-

### REFERENCES


