Oxygen Reduction Reaction Promotes Li$^+$ Desorption from Cathode Surface in Li-O$_2$ Batteries

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Li-O$_2$ batteries are claimed to be one of the future energy storage technologies. Great number of scientific and technological challenges should be solved first to transform Li-O$_2$ battery from a promise to real practical devices. Proposed mechanisms for oxygen reduction assume a reservoir of solved Li$^+$ ions in the electrolyte. However, the role that adsorbed Li$^+$ on the electrode surface might have on the overall oxygen reduction reaction (ORR) has not deserved much attention. Adsorbed Li$^+$ consumption is monitored here using impedance measurements from extended electrochemical double layer capacitance, which depends on the carbon matrix surface area. The presence of O$_2$ drastically reduces the amount of adsorbed Li$^+$, signaling the kinetic competition between Li$^+$ surface adsorption and its consumption, only for potentials corresponding to the oxygen reduction reaction. Noticeably double layer capacitance remains unaltered after cycling. This fact suggests that the ORR products (Li$_2$O$_2$ and Li$_2$CO$_3$) are not covering the internal electrode surface, but deposited on the outer electrode-contact interface, hindering thereby the subsequent reaction. Current results show new insights into the discharge mechanism of Li-O$_2$ batteries and reveal the evidence of Li$^+$ desorption from the C surface when the ORR starts.

1. Introduction

In an increasingly energy-dependent society, the need for renewable energy sources together to its storage is paramount to maintain current society paradigm in a sustainable way with the environment. Albeit Li-ion batteries (LIBs) have invaded the electronic market, their energy densities are usually limited below 250 Wh kg$^{-1}$.[1] This limitation is mainly originated by the mechanisms through which the chemical energy is stored in the present commercial LIBs that is based on the reversible reaction of the electrode materials with Li$^+$ ions by means of intercalation processes. Therefore, approaches based on new chemistry are necessary to increase the energy density in batteries, such as Li-S and Li-O$_2$, which can provide more than 1000 Wh kg$^{-1}$.[2] In particular, Li-O$_2$ batteries have received a great deal of attention as they can deliver the highest energy density among any other type of batteries. Li$^+$ ions and O$_2$ directly react with each other in the absence of any heavy transition metals or crystal framework.[3] Nevertheless, Li-O$_2$ battery technology is in its infancy and many fundamental issues are needed to be addressed before their practical application.

The chemical energy storage in Li-O$_2$ batteries is based on the oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) in the charge. $2\text{Li}^+ + \text{O}_2 + 2e^- \leftrightarrow \text{Li}_2\text{O}_2$ ($E^\circ = 2.96\,\text{V}$, with theoretical specific energy of 3500 Wh kg$^{-1}$). To date, Li$_2$O$_2$ has been identified as the main discharge product by different techniques such as Raman spectroscopy[4] and atomic force microscopy (AFM). Li$_2$O$_2$ is electronically insulating, very oxidative and insoluble, precipitating onto the electrode what causes the increase of the necessary potential for OER and the oxidation of the carbon electrode and/or electrolyte giving Li$_2$CO$_3$,[6] and as a consequence the decrease of the cycleability of the Li$_2$O$_2$ battery. Also, some authors note that the insulating nature of Li$_2$O$_2$ avoids its possible reduction to Li$_2$O, in this situation, Li$_2$O$_2$ batteries would provide energy densities as high as 5200 Wh kg$^{-1}$.[7]

It is then relevant that to fully exploit the capacity of Li$_2$O$_2$ batteries, the thermodynamic and kinetic mechanisms that govern and limit their functioning must be understood. From the pioneering studies of Abraham and co-workers[8] on the ORR to date, the oxygen reduction reaction has been widely analyzed in Li$_2$O$_2$ batteries,[9] and several models have been proposed, which have been recently unified by Bruce and co-workers.[10] Generally, the adsorption of O$_2$ molecules onto the cathode with one electron interchanged with the electrode is considered as the first step ($\text{O}_2 + e^- \leftrightarrow \text{O}^-_2$, $E^\circ = 2.71\,\text{V}$). This adsorbed O$_2^-$ reacts with Li$^+$ ions to produce LiO$_2$ adsorbed or as solid dissolved in the electrolyte. Depending on the solvent nature and the chemisorption strength with the cathode different mechanisms have been proposed for the reaction of the adsorbed LiO$_2$ with Li$^+$ ions until Li$_2$O$_2$ is reached as final product. In all these studies, the ORR starts with the reduction of oxygen in the context of free electrode surface and solved Li$^+$ ions in the electrolyte. However, the role that adsorbed Li$^+$ ions on the electrode surface might have on the overall ORR has not deserved much attention. This last contribution was pointed out by Qu and co-workers,[11] although no experimental evidence was provided. The monitoring for the first time of the desorption process of
Li$^+$ ions induced by ORR provides here revealing insights on the cathode surface processes in Li-O$_2$ batteries.

In this article, Li-O$_2$ discharge process in different cathodes has been monitored by electrochemical impedance spectroscopy (EIS). This technique has been recently used suggesting that the overpotential during discharge is caused by internal resistance, and is dominated by the charge transport through the deposited Li$_2$O$_2$ at the end of discharge.$^{[12]}$ Our study is based on a cathode made by carbon Super P with 30% of NiOCoO as catalyst in the presence and absence of O$_2$. Actually, both cathodes (with and without O$_2$) show the same impedance spectra from 4.0 to 2.7 V, in which extended electrochemical double layer capacitance (EDLC) made up by adsorbed Li$^+$ is observed. This capacitance has been verified on different systems and tested that is dependent on the surface area of the cathode. At lower voltages, the electrode in the presence of O$_2$ shows a huge capacitance increase at the same time that the EDLC is reduced. This fact evidences the depletion of the adsorbed Li$^+$ during the ORR. The results show three steps with their characteristic reaction time and resistance in the Li-O$_2$ discharge: (i) interfacial phenomena, (ii) EDLC, and (iii) chemical capacitance generated by oxygen reduction reaction (ORR capacitance). This study gives new insights on the Li-O$_2$ discharge mechanism provided by impedance spectra, and highlights the key contribution on the overall ORR of adsorbed Li$^+$ on the electrode surface.

2. Results and Discussion

2.1. Electrochemical Behavior in the Presence and Absence of O$_2$

Figure 1a shows the cyclic voltammetry (CV) of SP@30%NiOCoO in the presence of O$_2$ along different number of cycles and in the absence of O$_2$ (inset). Scan rate: 0.1 mV s$^{-1}$. The patterns of the pristine mesh, Li$_2$O$_2$, NiOCoO, and Li$_2$CO$_3$ are also shown.

Figure 1 shows the cyclic voltammetry (CV) of SP@30%NiOCoO in the presence of O$_2$ during cycling and in the presence of O$_2$ (inset). Scan rate: 0.1 mV s$^{-1}$. The pattern of the pristine mesh, Li$_2$O$_2$, NiOCoO, and Li$_2$CO$_3$ are also shown.

| Sample      | Species [% mol] |
|-------------|-----------------|
| 3 cycles, 2.4 V | 3.6 1.4        |
| 3 cycles, 3.4 V | 0.3 0.6        |
| 5 cycles, 3.4 V | 5.6 11.2       |
| 7 cycles, 3.4 V | 6.9 19.4       |

Table 1. Molecular percentage of Li in the form of Li$_2$O$_2$ and Li$_2$CO$_3$ determined by XPS (all data shown in the Supporting Information) in the sample cycles three, five or seven times at different stop voltage: 2.4 and 3.4 V.
carbon cathode and the electrolyte solvent in the presence of O₂, since carbon becomes unstable at voltages above 3.5 V. [16] At 2.6 V (and lower voltages), the Nyquist plot of the cathode in presence of O₂ changes drastically and the arc associated to the low frequency decreases dramatically. A new electrochemical feature is now observed at frequencies lower than 10 mHz (Figure 2f). This process should be related to the limiting step for ORR and O₂ diffusion. At high frequencies (above 5 Hz, Figure 2d–f), the Nyquist plots of the battery in absence of O₂ show one arc while there are two smaller arcs in the presence of O₂.

To gain deeper insight on the Li-O₂ discharge kinetics, the impedance data are represented in terms of capacitance (C = 1/iωZ) in Figure 3. In this representation, the real part, C', is related to the electrode charging while the associated resistance caused by kinetic limitations determines the value reached by the imaginary part, C". As explained elsewhere, [17] capacitive representation allows straightforwardly extracting contributing capacitors and, consequently, inferring on charging mechanisms. Each arc in a capacitance plot is assimilated to a RC series sub-circuit. In the region of low frequencies (below 5 Hz) an arc is observed that closes to ≈6.5 F g⁻¹ in the two systems (with and without O₂) within the voltage range 4.0–2.8 V. At lower voltages, a new arc is observed in the presence of O₂ that is more than two orders of magnitude higher than the previous one, and hides it. At high frequencies (see Figure SI.3, Supporting Information), smaller arcs linked to different capacitive features in the multi-step discharge process are observed for both systems, although the capacitance in presence of O₂ is larger than in its absence.

### 2.2. Electrode Mechanisms Through Equivalent Circuits

Figure 4a represents the capacitance spectra, C', versus characteristic time (inverse of measuring frequency) of the SP@30%NiOCoO cathode in the presence (solid lines) and absence (dashed lines) of O₂. The horizontal axis is also represented in frequency scale, inversely than usually drawn, from...
high to low frequency in order to maintain the same reading direction of the equivalent circuit model. In this representation, a plateau is demonstrative of a capacitive step in the discharge mechanism occurring at a certain frequency range. For electrodes with and without O$_2$, two plateaus are observed: the first one at intermediate frequencies ($\approx 100$ Hz) is O$_2$ dependent, while the second at low frequencies ($\approx 0.01$ Hz) is O$_2$ independent only at higher potentials. These two plateaus correspond to the two arcs described in Figure 3 and Figure SI.3, Supporting Information. The plateau at low frequencies is unaltered by the presence of O$_2$ in all the discharge process until 2.6 V. Noticeably below this potential the presence of O$_2$ induces the capacitance decreasing by one order of magnitude showing a plateau that ends at 10 mHz. At lower frequencies the capacitance further increases in relation to the diffusion and reaction process discussed in Figure 2f.

By observing Figure 4a one can distinguish three steps in the discharge process, which are marked with squares and represented in the different subcircuits of the equivalent circuit model shown in Figure 4b. The fitting of the proposed equivalent circuit model is represented in Figures 2 and 3 with solid lines. The observed steps during discharge are:

(i) Interfacial phenomena (high frequency: $>5$ Hz) that is O$_2$ dependent. In the presence of O$_2$ two arcs are observed in the Nyquist plot, which are represented by two resistances ($R_{i1}$ and $R_{i2}$) in parallel with two capacitances ($C_{i1}$ and $C_{i2}$). In the absence of O$_2$, only one arc is observed that is equivalent to a resistance ($R_{i}$) in parallel to the capacitance ($C_{i}$).

(ii) EDLC (intermediate frequency: $10$ mHz < $f$ < 5 Hz) that is O$_2$ independent at high potentials. This mechanism is connected to the Li$^+$ adsorption on the internal electrode surface. This capacitance, $C_{EDL}$, is associated to an arc in the $C''$ versus $C'$ representation that can be modeled by a series $RC$ circuit.\cite{17,18} The associated resistance $R_{ads}$ accounts for the Li$^+$ transport in the electrolyte within the porous matrix. More details of this subcircuit model are in the Supporting Information.

(iii) Chemical ORR capacitance (low frequency: $<10$ mHz) that only appears in the presence of O$_2$. When O$_2$ starts to react (at 2.8 V and below) a new parallel branch to the EDLC is represented in the equivalent circuit model by the chemical capacitance, $C_{ORR}$, in series to the associated resistance, $R_{ORR}$, accounting for the reduction reaction.

2.3. Interfacial Phenomena

The electrochemical processes related to the interface are monitored by EIS at high frequencies. In the absence of O$_2$, a single semicircle is observed in the Nyquist representation (Figure 2 d–f) that is associated with a semicircle to the $C''$ versus $C'$ representation, Figure S13, Supporting Information. This capacitance, $C_{i}$, and resistance, $R_{i}$, can be associated to the impedance generated at the contact interface between the electrode and the electrolyte solution.\cite{19} In the presence of O$_2$, two small arcs are distinguished in Figure 2 d–f. One of the arcs can be ascribed to the formation of the insulating layer made up of Li$_2$O$_2$ and Li$_2$CO$_3$ (as XPS and XRD shown), and

Figure 4. a) $C'$ versus characteristic time and frequency (in opposite order than usual, from fast to slow electrochemical processes for a more intuitive reading) for SP@30%NiOCoO in the presence (solid lines) and absence (dashed lines) of O$_2$. Inset: Scheme of the three processes of the Li–O$_2$ discharge mechanism. The ORR is represented on the cathode surface by a graphitic layer, in which adsorbed Li$^+$ react with O$_2$. b) Equivalent circuit model for the system in the absence and presence of O$_2$. 

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the other to the impedance at the contact interface, as it has been assigned in the absence of O₂. In any case these resistive elements introduce limitations into the overall charging mechanism.

The fitting values obtained by the equivalent circuit model are represented in Figure 5. With the calculated values, we can indicate that C₁₂ and R₁₂ are related to the electrode/electrolyte contact since they are constant independently of the applied voltage. In this assumption, C₁₁ and R₁₁ should be related to the solid electrolyte interface (Li₂O₂ and Li₂CO₃) formed on the cathode, which explains why the capacitance increases with the oxygen reduction reaction.

2.4. Electrochemical Double Layer Capacitance

With the equivalent circuit model (Figure 4b), the main parameters of the Li⁺ adsorption step in the discharge process are obtained, Figure 5. In the absence of O₂, the capacity is practically constant, 6.5 F g⁻¹ (that corresponds to ≈8 µF cm⁻² considering an area S_BET = 75 m² g⁻¹), independently of the voltage. This value is within the range of reported electrochemical double layer capacitances in supercapacitors based on carbon materials (5–20 µF cm⁻²) [13a]. In this case, the capacitance is in agreement with a lower value obtained with supercapacitors when an organic electrolyte is used compared to aqueous electrolytes [20]. Associated to the charge accumulation by physical electroadsorption there is a resistance that has been related to the ion transport along the tortuous path of the micro/mesoporosity of the carbon matrix [21]. In the presence of O₂, the EDL capacitance is unaltered at high voltages and noticeably decreases when the ORR starts. This is in accordance with recent capacitance analyses [12]. The resistance of the Li⁺ adsorption process consistently increases, showing the kinetic competition between Li⁺ adsorption and consumption by ORR at voltages lower than 2.8 V. At the same time, the parallel resistance, R_ORR, decreases dramatically (close to three orders of magnitude) giving further support to the idea that the current runs along the parallel branch corresponding to the ORR subcircuit in Figure 4b. At lower voltages than ORR reaction, (i.e., 2.2 V), the capacitance of the EDL starts to increase again signaling a full recovering of the double layer features. We infer that the ORR branch in Figure 4b is kinetically favored at potentials 2.4–2.8 V.

To check the role of species involved in the EDLC formation as a step in the discharge mechanism, other systems have been measured for consistency. The same results have been obtained in the absence of catalyst (Figure SI.4, Supporting Information) and the study with carbons of different S_BET has revealed that EDLC can be considered only dependent on the carbon surface area (Figure SI.5, Supporting Information). This point is further discussed in the Supporting Information since depending on the size of the pores the area can be active or not to the formation of the EDL like in the case of supercapacitors.

In order to analyze the effect of cycling on the formation of the electric double layer, the electrochemical impedance spectrum at 3.4 V (during lithiation process) has been registered along several CV cycles. The Nyquist and capacitance plots are represented in Figure 6 and the obtained fitting parameters in
property is not modified after cycling, and Li cycling number. This result shows that the electrode textural capacitances practically constant, independently of the potential limitation and the cause of the low rechargeability of the products (Li$_2$O$_2$ and Li$_2$CO$_3$) are not covering the internal electrode face of the cathode is considered as a raw graphitic layer where the Li$^+$ ions arrive from the electrolyte side. This study demonstrates that the surface is already covered by adsorbed Li$^+$ when ORR starts, what it could imply that for the soluble O$_2$ to react with Li$^+$, the molecular O$_2$ can first react with the adsorbed Li$^+$ on the surface nearly the outer O$_2$ entrance layer, forming Li$_2$O$_2$ and avoiding further reaction. Qu and co-workers$^{[21]}$ reported that the discharge capacitance can be increased with O$_2$ pressure higher than 1 atm since the electrolyte was forced back from the interface and the complete wetting of the cathode is avoided. Therefore, adsorbed Li$^+$ consumption provides a new context of the cathode surface where the oxygen reduction reaction develops.

2.5. ORR Capacitance

At low voltages the reduction reaction of O$_2$ takes place. ORR is the main process in Li$_2$O$_2$ batteries that provides the unique high capacity, but the main drawback for following this reaction by EIS is its extremely slow rate; it is registered at frequencies below 10 mHz. For this reason, the fitting of the data is only partial. In Figure 4b it has been represented by a resistance in series with the chemical capacitance for the purpose of clarity. Nevertheless, in the Nyquist plot is observed that the real part of the impedance (−Z’) increases, then signaling an extra resistive behavior in addition to the capacitive one observed in Figure 4a. For this reason, more elements than the chemical capacitance are certainly needed. It is indeed the final limiting step related to the O$_2$ diffusion through different layers. It is obvious that it is necessary to fast up this process in order to make it fully observable by impedance methods.

3. Experimental Section

All the agents were purchased from Sigma Aldrich, and were used as received. The cathodes were prepared by painting a carbon/PVdF slurry onto a stainless steel mesh. The slurries were prepared by mixing carbon black/PVdF/catalyst (60:10:30% wt) and the addition of 1-methyl-2-pyrrolidone. All the cathodes were dried in vacuum, at 110 °C overnight. Mixed-metal oxides are proved to be good catalysts for both ORR and OER in Li$_2$O$_2$ batteries.$^{[24]}$ In this study, a commercial nanopowder, nickel cobalt oxide, (of size lower than 150 nm, CAS 5859–45–0, Sigma-Aldrich) was observed to accelerate H$_2$O$_2$ oxidation (Figure S1.8, Supporting Information) and, consequently, it is a good candidate as catalyst for Li$_2$O$_2$ batteries,$^{[25]}$ albeit no reference of its use has been found in the literature. Despite its study is out of the topic of this article, we have seen that its main contribution is the reduction of the charge transfer resistance (Figure S1.9, Supporting Information).

Cell assembly (Swagelok type) was carried out in a N$_2$ filled glovebox. This consists simple in clamping together a Li metal foil anode, an electrolyte-soaked separator, the electrolyte that is 1 M hexafluorophosphate lithium salt ([LFPF$_6$]$_x$) dissolved in tetraethylene glycol dimethyl ether (TEGDME), the cathode under study and the stainless steel current collector. The cathode collector is a tube in which the discharge capacitance can be increased with O$_2$ pressure higher than 1 atm since the electrolyte was forced back from the interface and the complete wetting of the cathode is avoided. Therefore, adsorbed Li$^+$ consumption provides a new context of the cathode surface where the oxygen reduction reaction develops.

![Figure 6. a) Nyquist and b) Capacitance plots of the SP@30%NiOCoO air cathode at 3.4 V at different number of CV cycles.](image-url)
this voltage range with an amplitude perturbation of 10 mV, and in the frequency range of 1 MHz to 1 mHz. The approximation to the different voltages of measurement was potentiostically controlled at 10 µV s⁻¹ to assure the quasi-equilibrium state of the battery. Also, before each measurement the system was stabilized during 30 min. All the data are normalized to the carbon mass.

The cycled electrodes were characterized by means of X-ray powder diffraction (XDR) using Bruker AXS-D4 Endeavor Advance X-ray diffractometer using CuKα radiation. X-ray photoelectron spectroscopy (XPS) was performed on Sage 150 de Spectra with non-monochromatic radiation AlKα (1486.6 eV) to 20 mA and 13 kV, a constant pass energy 75 eV for global analysis and 30 eV for specific binding energy of each element analysis, and an area measuring 1 x 1 mm². The base pressure of XPS chamber was 7 x 10⁻⁸ hPa. XPS spectra were fitted with CasaXPS software, which models the Gaussian-Lorentzian contributions, after background subtraction. Also, energy spectra were calibrated by setting the C 1s photoemission peak for sp²-hybridized carbon to 284.8 eV. Samples were washed out by anhydrous dimethyl carbonate (DMC, Sigma-Aldrich) solvent several times, and dried in a vacuum chamber at 60 °C for 2 h previous XRD and XPS measurements.[26]

4. Conclusions

This article analyzes the discharge process of Li-O₂ batteries by impedance spectroscopy and provides a novel equivalent circuit model. In this model, different electrochemical processes during discharge mechanism are identified: (i) interfacial phenomena, (ii) EDLC, and (iii) ORR chemical capacitance. EDLC has been monitored in Li-O₂ batteries and it is observed to be independent of the presence of O₂ at voltages higher than those at which oxygen reduction reaction occurs. Noticeably EDLC is fully recovered after electrode charging, and remains unaltered after cycling. This fact suggests that the ORR products (Li₂O₂ and Li₂CO₃) are not covering the internal electrode surface, but deposited on the outer electrode-O₂ interface, hindering thereby the subsequent reaction. At this moment, further research is necessary to elucidate if these adsorbed Li⁺ at the internal electrode double layer can directly react with the O₂ molecules at the voltage where ORR starts or they are merely displaced by the reduction of O₂ molecules. The novel equivalent circuit model and the consideration that Li⁺ ions are already adsorbed on the carbon surface when ORR starts provide new tools in the study and design of Li-O₂ cathodes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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