

Oxygen Reactions in a Non-Aqueous Li⁺ Electrolyte**

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Oxygen (O₂) reduction is one of the most studied reactions in chemistry.^[1] Widely investigated in aqueous media, O₂ reduction in non-aqueous solvents, such as CH₃CN, has been studied for several decades.^[2–7] Today, O₂ reduction in non-aqueous Li⁺ electrolytes is receiving considerable attention because it is the reaction on which operation of the Li–air (O₂) battery depends.^[8–29] The Li–O₂ battery is generating a great deal of interest because theoretically its high energy density could transform energy storage.^[8,9] As a result, it is crucial to understand the O₂ reaction mechanisms in non-aqueous Li⁺ electrolytes. Important progress has been made using electrochemical measurements including recently by Laoire et al.^[29] No less than five different mechanisms for O₂ reduction in Li⁺ electrolytes have been proposed over the last 40 years based on electrochemical measurements alone.^[25–29] The value of using spectroelectrochemical methods is that they can identify directly the species involved in the reaction. Here we present in situ spectroscopic data that provide direct evidence that LiO₂ is indeed an intermediate on O₂ reduction, which then disproportionates to the final product Li₂O₂. Spectroscopic studies of Li₂O₂ oxidation demonstrate that LiO₂ is not an intermediate on oxidation, that is, oxidation does not follow the reverse pathway to reduction.

In this work CH₃CN was used as the solvent because it has been used widely for O₂ reduction and shown to be sufficiently stable towards reduced O₂ species for the studies undertaken herein.^[4,5] Au was chosen as the electrode because it is an excellent substrate for surface enhanced

Raman spectroscopy (SERS).^[30] To confirm that the electrode/electrolyte combination used herein is sufficiently stable for our studies, cyclic voltammograms (CVs) were collected in 0.1 M *n*Bu₄NClO₄–CH₃CN saturated with O₂ at an Au electrode (Figure S1 in the Supporting Information). These data show that Q_A/Q_C ≈ 1 (Q is the charge passed on the anodic (A) and cathodic (C) sweeps, see Table S1) at all scan rates in Figure S1, in accord with the reversibility and hence stability of the electrolyte and electrode towards the reduced O₂ species.

O₂^{•−} has been detected previously in CH₃CN.^[4] To confirm its formation on reduction of O₂ in our experiments, in situ SERS data were collected on the Au electrode in 0.1 M *n*Bu₄NClO₄–CH₃CN at various potentials on reduction and oxidation, indicating respectively the formation of O₂^{•−} and its disappearance (Figure 1). The peak assignments in Figure 1

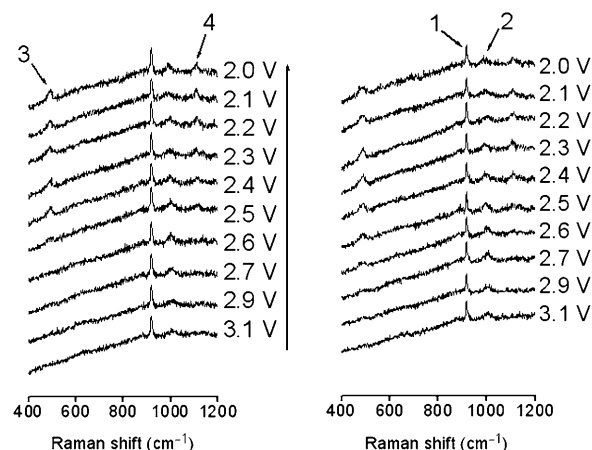


Figure 1. In situ SERS of superoxide. Spectra were obtained from a roughened Au electrode in O₂ saturated 0.1 M *n*Bu₄NClO₄–CH₃CN. The cathodic potential sweep from 3.1 V to 2.0 V vs Li/Li⁺ is shown on the left, while the anodic sweep is shown on the right. Peak assignments are as follows: 1) C–C stretch of CH₃CN at 918 cm^{−1}, 2) N–(C₄)₄ stretch of *n*Bu₄N⁺ at 996 cm^{−1}, 3) Au–O stretch of adsorbed O₂^{•−} at 491 cm^{−1}, 4) O–O stretch of adsorbed O₂^{•−} at 1109 cm^{−1}.

were based on the vibrational spectrum for O₂^{•−}^[4a] and the SERS spectrum in Figure S2; the data for the latter were obtained by dissolving KO₂, using a crown ether to complex the K⁺ and hence promote dissolution (see caption to Figure S2). The CVs of O₂ reduction as a function of scan rate were analyzed using the DigiSim software.^[31] The heterogeneous rate constant, $k^0 = 2.1 \times 10^{-4} \text{ cm s}^{-1}$, was obtained from this analysis. The O₂ concentration [O₂] = 6.8 mM and O₂ diffusion coefficient $D_{\text{O}_2} = 7.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$

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were obtained by fitting the current response to a potential step at an Au microelectrode (Figure S3) following the procedure described previously^[7] (see Experimental Section). It is known that O_2^- can form ion pairs with molecular cations such as organic ammonium ions, however, such interactions are weak compared with those involving Li^+ ions.^[2,26]

The reaction between O_2^- and Li^+ was investigated as a function of Li^+ concentration (Figure 2). Addition of a 1 mM concentration of Li^+ resulted in the appearance of a new

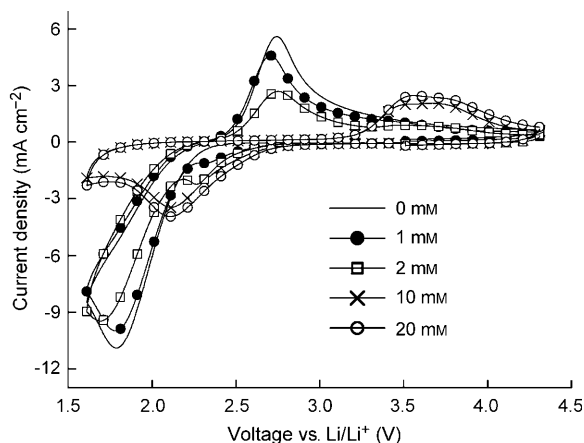


Figure 2. Cyclic voltammetry at an Au electrode in O_2 -saturated 0.1 M $n\text{Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ containing various concentrations of LiClO_4 as indicated. The scan rate was 1.0 V s^{-1} because at this rate the reduction to O_2^- and LiO_2 as a function of Li^+ concentration can be seen most clearly.

reduction peak at higher potentials (2.35 V) compared with the original O_2 reduction peak. The magnitude of the new peak grows with increasing Li^+ concentration and at the expense of the area under the original O_2 reduction peak. This behavior is consistent with an EC mechanism, that is, electrochemical reduction followed by a chemical step.^[32] Such following chemical reactions severely deplete the concentration of O_2^- thus shifting the potential to higher voltages, as observed here.^[32] When the concentration of Li^+ ions is lower than O_2 , then there is insufficient Li^+ to react with all the O_2^- that is generated, hence “unbond” O_2^- persists and two peaks are apparent. When the concentration of Li^+ exceeds that of O_2 (in this case the O_2 concentration is 6.8 mM) then all the O_2^- is consumed by reacting with Li^+ . The low voltage reduction peak disappears leaving only one reduction peak. For a similar reason the peak at 2.75 V associated with O_2^- oxidation disappears when the Li^+ concentration exceeds that of O_2 . The shift of the reduction potentials to lower voltages and the lowering of the reduction current with increasing Li^+ concentration are consistent with partial blockage of the electrode surface by the insulating reduction products, which becomes more severe at higher Li^+ concentrations. Such a phenomenon has been observed before.^[27] As stated above, Au was used because it permits SERS studies of the electrode surface. The same electrochemical reactions occur on glassy carbon electrodes, as shown in Figure S4.

Although these and previous electrochemical studies are very valuable, they cannot identify directly the species formed on reduction. This is illustrated by the fact that different authors have proposed different mechanisms for O_2 reduction based on electrochemical measurements;^[25–29] two examples are given here:



or



Spectroscopic methods can identify directly the reaction products and their intermediates, and therefore are invaluable in investigating the O_2 reduction mechanism. The results of in situ SERS measurements are presented in Figure 3. A

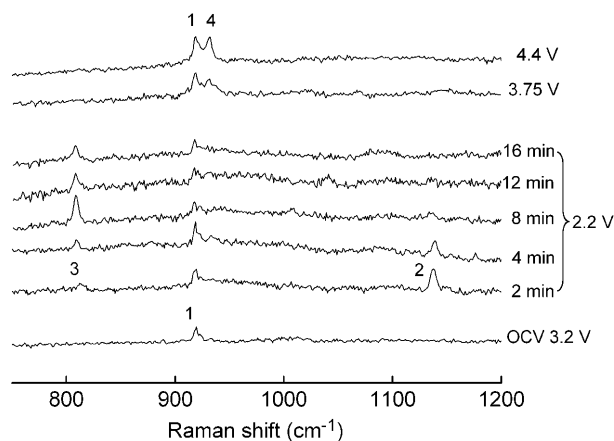


Figure 3. In situ SERS during O_2 reduction and re-oxidation on Au in O_2 -saturated 0.1 M $\text{LiClO}_4\text{-CH}_3\text{CN}$. Spectra collected at a series of times and at the reducing potential of 2.2 V versus Li/Li^+ followed by other spectra at the oxidation potentials shown. The peaks are assigned as follows: 1) C–C stretch of CH_3CN at 918 cm^{-1} , 2) O–O stretch of LiO_2 at 1137 cm^{-1} , 3) O–O stretch of Li_2O_2 at 808 cm^{-1} , 4) Cl–O stretch of ClO_4^- at 931 cm^{-1} .

background spectrum was collected before application of a potential to the cell (OCV; open circuit voltage). The spectrum is consistent with that expected for CH_3CN ; the peak (1) at 918 cm^{-1} is assigned to the C–C symmetric stretch in CH_3CN . Data were then collected at a potential of 2.2 V, that is, within the reduction peak in Figure 2. Spectra are shown at this potential for successive time intervals. Within a short time, two new peaks (2 and 3) appear that were not present at OCV. The most prominent occurs at 1137 cm^{-1} and is associated with the O–O stretch of LiO_2 .^[33,34] The smaller peak at 808 cm^{-1} corresponds to the O–O stretch of adsorbed Li_2O_2 .^[35,36] With the passage of time the LiO_2 peak diminishes until only the Li_2O_2 peak remains. The LiO_2 peak occurs some

28 cm⁻¹ higher than O₂⁻ in *n*Bu₄N⁺ solution, in accord with the stronger binding of O₂⁻ to Li⁺ in LiO₂, resulting in the transfer of anti-bonding electron density from O–O⁻ to Li⁺. The Raman spectra provided direct spectroscopic evidence that reduction of O₂ in the presence of Li⁺ ions in a non-aqueous electrolyte first forms O₂⁻ that then binds to Li⁺ forming LiO₂ on the surface of the electrode. They further demonstrate that LiO₂ is unstable and disproportionates to the more stable Li₂O₂, that is, 2LiO₂ → Li₂O₂ + O₂. In other words the Raman spectra have shown that the process of O₂ reduction in the presence of Li⁺ follows Equations (2a–c) described above, and *does not* proceed through disproportionation of superoxide to peroxide ions [Equations (1a,b)] followed by the formation of Li₂O₂ without passing through LiO₂ as an intermediate.^[25–29] It also shows that the LiO₂ intermediate is present on the electrode surface. It is known that on extending the voltage range to much more cathodic potentials further reduction process occurs that may be assigned to O₂⁻ reduction to O₂²⁻ in the absence of Li⁺.^[2,3] In the presence of Li⁺, LiO₂ reduction to Li₂O₂ occurs (Figure S5). However, this is at a significantly more negative (lower) potential than the SERS data (0.8 V lower), thus direct reduction of LiO₂ to Li₂O₂ is unlikely to make a major contribution to the transformation of LiO₂ to Li₂O₂ at the voltages used in our experiments, which instead are dominated by disproportionation.

Returning to the CVs in Figure 2, at high Li⁺ concentrations two oxidation peaks are apparent at 3.55 and 3.75 V. To investigate the oxidation in more detail, a series of CVs was collected in 0.1M LiClO₄-CH₃CN (Figure 4). Each CV

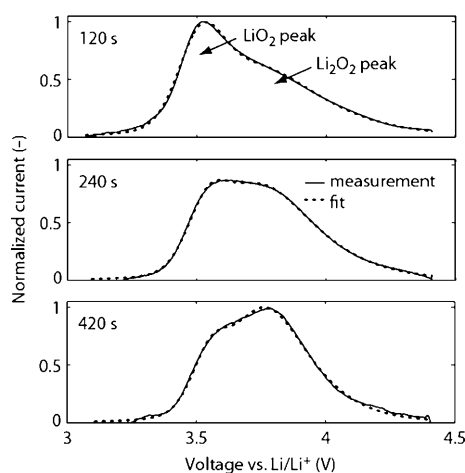


Figure 4. Oxidation waves on Au in 0.1 M LiClO₄-CH₃CN after various dwelling times at OCV. Before the dwelling, the potential was swept from 3.2 V to 2.2 V to form the reduction products, LiO₂ and Li₂O₂, scan rate 1.0 V s⁻¹.

was collected by first sweeping the potential from 3.2 V (OCV) to 2.2 V and then keeping the potential at OCV for various dwell times, before completing the oxidation sweep. Sweeping the potential to 2.2 V results in the formation of LiO₂ and Li₂O₂. Thereafter, short dwell times lead to the presence of the lower voltage oxidation process, whereas this

peak diminishes as the high voltage peak grows with increasing dwell time. The lower voltage oxidation peak is associated with the oxidation of LiO₂, whereas longer dwell times result in a proportionately greater quantity of Li₂O₂, the decomposition of which is associated with the high voltage oxidation peak. The purpose of the dwell time experiments was to investigate the kinetics of disproportionation: by employing various dwell times and deconvoluting the areas under the two oxidation peaks (see Experimental Section), the first-order rate constant for the disproportionation reaction from LiO₂ to Li₂O₂ + O₂ was calculated, $k = 2.9 \times 10^{-3} \text{ s}^{-1}$.

The presence of oxidation peaks for both LiO₂ and Li₂O₂ in the CVs only occurs because of the relatively short time scales. In practice, Li–O₂ cells are charged and discharged over much longer times, and hence all the LiO₂ will have disproportionated to Li₂O₂ by the end of discharge. Therefore, in the context of the Li–O₂ battery, it is interesting to examine the oxidation (charging) of pure Li₂O₂. As for reduction, different mechanisms may be proposed for oxidation of Li₂O₂; for example one mechanism involves the oxidation of Li₂O₂ to LiO₂ then to O₂ [Equations (3a,b)], but others are also possible, such as Equation (4), which does not involve LiO₂ as an intermediate.



or



As noted above, the oxidation peak for Li₂O₂ occurs at 3.75 V, which is above the oxidation potential for LiO₂ at 3.5 V, leading us not to expect LiO₂ as an intermediate on oxidizing Li₂O₂ since LiO₂ would be unstable at 3.75 V. However, to explore this directly, in situ SERS and in situ differential electrochemical mass spectroscopy (DEMS) data were obtained. Considering first the Raman data: after applying a reducing potential of 2 V until only Li₂O₂ was present, the potential was switched to 3.75 V (the oxidation potential of Li₂O₂) then to 4.4 V. The SERS spectra collected at these oxidation potentials are shown in Figure 3, and there is no evidence of LiO₂, consistent with Li₂O₂ decomposing directly without passing through LiO₂ as an intermediate. It has recently been confirmed that O₂⁻ reacts strongly with propylene carbonate electrolytes to form various decomposition products including CO₂.^[37] As a result we can now use this electrolyte as a chemical probe for superoxide: if oxidation of Li₂O₂ formed LiO₂ or O₂⁻ then in PC electrolyte CO₂ would be observed. An electrode was constructed in the discharged state, that is, containing Li₂O₂ (Aldrich), then placed in contact with a 0.1M solution of LiPF₆ in propylene carbonate. The electrode was charged in successive current steps, the results are presented in Figure S6. As the current is increased there is an immediate increase in the cell potential and a corresponding increasing in the *m/z* = 32 signal due to O₂ evolution on decomposing Li₂O₂ upon charging. No other gases are evolved at a level greater than 1 % of the O₂. In

particular, the absence of a mass signal at $m/z = 44$, corresponding to CO_2 , indicates that Li_2O_2 decomposes directly in a one-step process to $\text{Li}^+ + \text{e}^- + \text{O}_2$, that is, through Reaction (4). O_2 evolution upon charging Li_2O_2 has been reported earlier,^[11] however, the sensitivity of the former DEMS apparatus did not allow the detection of minority gases. Here we have used a new generation of DEMS apparatus (developed by one of us; P.N.), with gas detection limits improved to low ppm values thus making possible detection of CO_2 , and hence superoxide (if present), down to a level of 0.1% of O_2 . Together, the SERS and DEMS results demonstrate that oxidation occurs by direct decomposition according to the reaction $\text{Li}_2\text{O}_2 \rightarrow 2\text{Li}^+ + 2\text{e}^- + \text{O}_2$. In other words, the pathways followed on reduction and oxidation are different. This is in accord with the different voltages for charge and discharge, the separation of which persists even at low charge/discharge rates as confirmed by the CV with low scan rate in Figure S7. The different pathways for reduction and oxidation do not violate the principle of microscopic reversibility. The discharge reaction is in three steps and may be viewed as an ECC mechanism [Equations (2a–c)]. For microscopic reversibility, the reaction on charging would have to reverse along the same path, that is, CCE. As reduction occurs at 2.2 V and oxidation of Li_2O_2 at approximately 3.7 V, even at low rates, as discussed above, this implies that at least one of the forward reaction steps, most likely reaction step (2c), is irreversible or at least the reverse chemical reaction is very slow. As a result, direct electrochemical oxidation of Li_2O_2 occurs more readily than reversing along the same pathway as reduction. This phenomenon has been discussed before, all be it in quite different systems such as reductive decomposition of alkylhalides.^[38]

In conclusion, in situ spectroscopic studies of O_2 reduction in non-aqueous solvent, in the presence and absence of Li^+ ions, have provided direct evidence of LiO_2 as an intermediate on O_2 reduction, which then disproportionates to Li_2O_2 ($k_{\text{dispr.}} = 2.9 \times 10^{-3} \text{ s}^{-1}$). On charging, in situ spectroscopic studies reveal that Li_2O_2 decomposes directly, in a one-step reaction to evolve O_2 and does not pass through LiO_2 as an intermediate.

Experimental Section

CH_3CN was distilled then further dried for several days over freshly activated molecular sieves (type 4 Å) resulting a final water content of ≤ 4 ppm (determined using a Mettler-Toledo Karl Fischer titration apparatus). Electrochemical grade $n\text{BuNClO}_4$ and battery grade LiClO_4 were used for preparing the electrolytes as they can be obtained in high purity. Prior to use, both $n\text{BuNClO}_4$ and LiClO_4 were dried by heating under vacuum at 80 and 160 °C, respectively, for 24 h. Electrochemical measurements were conducted in a multi-necked, air-tight glass cell with valves to control the gas inlet and outlet. A polycrystalline Au disk (BAS Inc.) electrode (diameter 1.6 mm or 10 μm for ultra-microelectrode) was used as the working electrode and was polished with 0.05 μm alumina slurry prior to use. The surface area of the ultra-micro Au working electrode was quantified by steady state polarization in 0.5 M $n\text{BuNBF}_4\text{-CH}_3\text{CN}$ containing 1.0 mM ferrocene (Fc) using the known diffusion coefficient, $D = 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, for Fc.^[39a] Diffusion coefficient and solubility of O_2 was extracted from the potential step at an Au microelectrode using the nonlinear curve fitting function in Origin 6.1 (Originlab Co.)

following the equations proposed by Shoup and Szabo.^[39b] A platinum wire served as the counter electrode. A silver wire immersed in a glass tube containing the supporting electrolyte, separated from the main solution by a porous glass frit, was used as the quasi reference electrode, which was calibrated with the Fc^+/Fc couple, itself calibrated versus $\text{Li}/\text{Li}^+(1.0 \text{ M})$ in propylene carbonate (PC). Electrochemical measurements were carried out at room temperature using an Autolab PG30 electrochemical workstation. Deconvolution of the two oxidation peaks for the dwell time experiments was carried out using customized code written within the Matlab software package. A linear combination of Gaussian and Cauchy distributions was used to describe the peaks. The background was determined by an oxidation sweep without prior reduction sweep.

The electrochemically roughened Au working electrode^[40] was placed behind a 1 mm thick sapphire window with the reference and counter electrodes identical to those described above. Raman spectra were recorded using a customized Renishaw Raman system with an excitation wavelength of 632.8 nm. The collection optics is based on a Leica inverted microscope with a 50 $\times$ objective lens. The power of the laser beam delivered to the electrode surface is estimated to be 2.5 mW and the spectrum acquisition time is typically 30 s.

The cell exploring charging of chemical Li_2O_2 consisted of a lithium anode, electrolyte (0.1 M LiPF_6 in PC) impregnated into a glass fiber separator, and a porous cathode containing the Li_2O_2 . The porous cathode consisted of carbon black (Super P, TIMCAL), $\alpha\text{-MnO}_2$ nanowires, polyvinylidene fluoride (Kynar) (mol ratios of 95:2.5:2.5) and chemical Li_2O_2 . The cell was purged continuously with Ar gas which flowed from the cell into the mass spectrometer carrying the evolved gases for mass analysis. The experiment setup is described in detail elsewhere.^[41]

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