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Electrochemical Cells

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Investigation of the O_2 Electrochemistry in a Polymer Electrolyte Solid-State Cell**

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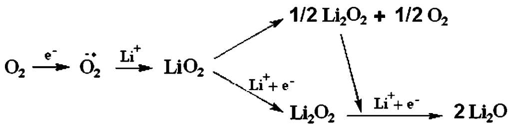
The oxygen electrode has been the subject of intense activity for more than 150 years, since the report of the first fuel cell in 1842 by Grove.[1] Recently, there had been a revived interest in the utilization of air as oxidizer in the positive electrode of air secondary batteries, for example, lithium–air batteries. Very high specific energies can be obtained from these systems (at 2 kWh$\,$kg^{-1} of reactant for lithium), and these high numbers justify the present excitement for the lithium–air battery. While systems in which lithium is totally protected from the outside environment by an impervious vitroceramic electrolyte[2] are akin to fuel-cell electrodes as the medium is aqueous, a good fraction of relevant research is geared towards the implementation of a reversible O_2 electrode in organic aprotic solvents that are somehow compatible with lithium.[3–11]

In contrast with aqueous systems, in which the ultimate reduction product requires four electrons, to H_2O or OH^-, the most often observed product in dismantled electrodes or in situ observations of Li/O_2 organic electrolyte batteries is Li_2O_2 ($E_o = 2.96$ V), that is, there is no cleavage of the O–O bond. It is well known that in aprotic systems the oxygen molecule is easily, and in some solvents reversibly, reduced to the radical anion $O_2^{-\cdot}$, provided that the counterion is a large cation of "onium" type (e.g. tetrabutylammonium) or even heavier alkali ions.[9,12] In the presence of a more polarizing countercation, $O_2^{-\cdot}$ rapidly disproportionates or accepts another electron. Accordingly, the reduction of molecular oxygen in aprotic solvents may be assumed to proceed as in Scheme 1.



Scheme 1. Oxygen-molecule reduction in aprotic systems.

Most research on the Li–air system has focused on the capacity, expressed per gram of carbon used as collector in the positive electrode. This approach has several drawbacks, as the electrically insulating products Li_2O_2 and Li_2O, besides mechanically clogging the electrode owing to insolubility, impair the diffusion of oxygen and of electrolyte, and the polarizations observed are difficult to translate into a particular electrode process.[13] Moreover, the choice of electrolytes is often questionable. O_2^-, O_2^{2-}, and O^{2-} are very strong bases, with pK_A values close to 30 and 40 on the Bordwell DMSO acidity scale that has to be used in aprotic media, and all three are very strong nucleophiles. As now demonstrated by various authors, the "unsinkable" carbonate esters should be avoided totally,[3,14,15] and even the almost universal solvent DMSO would be deprotonated by "naked" O_2^{2-} and O^{2-} if the very small solubility product of the Li salt did not prevent such reaction. The solute anion PF_6^- is also prone to substitution, given the polarity and lability of the P–F linkage.

These issues hamper the study of the electrochemical processes of the oxygen electrode in cells using conventional carbonate ester electrolytes. Herein we depart totally from this conventional approach by moving to a solid-state cell using a poly(ethylene oxide)–lithium triflate (PEO-$LiCF_3SO_3$) solvent-free polymer electrolyte. The main purpose was to assure a cell structure in which reactions of the products of the electrochemical process (and, particularly, of the singlet oxygen) with electrolyte could be totally avoided. Therefore, PEO-based electrolytes were chosen, as the resistance of the PEO ether linkage is well-documented (e.g. Grignard reagents) and $LiCF_3SO_3$ is stable towards nucleophiles, especially under the low current densities used in this study. PEO, owing to the tendency of the polymer to arrange into *trans-gauche-trans* helices to accommodate ions, is far more solvating in the solid state than even its shorter liquid homologues, such as the recently used tetraglyme.[9] Another advantage of the solid state is the stability of the triple contact between the carbon, the electrolyte, and the surrounding O_2, especially under low charge passage. The main goal of this work is then to use a PEO-based Li–O_2 solid-state cell to investigate the electrochemical processes occurring at the oxygen electrode. It is expected that, owing to the favorable properties of the solid electrolyte, the cell is able to provide reliable results.

The PEO-based polymer electrolyte, hereafter referred to as PCE (polymer composite electrolyte), the cell configuration, and the experimental setup are described in detail in the Experimental Section. Our study was performed using electrochemical techniques, in particular potentiodynamic cycling with galvanostatic acceleration (PCGA) and cyclic

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voltammetry (CV) analyses on the solid-state cell. PCGA is a quasi-equilibrium technique that can provide very useful detailed information of electrochemical processes[16–18] by analyzing the integral of the current during the step time (δQ) reported versus the cell potential in the same step. Figure 1 A reports the potential (left) and the current (right) versus the capacity (normalized by the mass of the carbon), and Figure 1 B shows the incremental charge δQ versus the potential profile of the PCGA trace obtained for our Li/PCE/SP-carbon,O_2 cell (see Experimental Section). The current trend in Figure 1 A strongly suggests that the electrochemical process takes place according to a multistep mechanism, depending on the charge regime. Indeed, Figure 1 B shows a starting open-circuit voltage of 3.2 V versus Li and at least three peaks in the cathodic scan (reduction) and three peaks in the anodic scan (oxidation).

During the reduction process[1] we can distinguish two overlapping peaks at 2.7 and 2.65 V versus Li, likely corresponding to the reactions $O_2 + e^- + Li^+ \rightarrow LiO_2$ and $LiO_2 + e^- + Li^+ \rightarrow Li_2O_2$, respectively. A further sharp reduction peak is observed at 2.63 V, which is probably associated with the reaction $Li_2O_2 + 2e^- + 2\,Li^+ \rightarrow 2\,Li_2O$ (or with the reaction $1/2\,Li_2O_2 + 1/2\,O_2 + 3\,e^- + 3\,Li^+ \rightarrow 2\,Li_2O$), see Scheme 1. This mechanism is supported by literature data[2,19] as well as by ex situ X-ray analysis carried out at the end of the cell process, which confirmed the presence of the assumed products of oxygen reduction in our system, that is, Li_2O_2 and LiOH, the latter of which likely results from the reaction of Li_2O with residual water impurities.

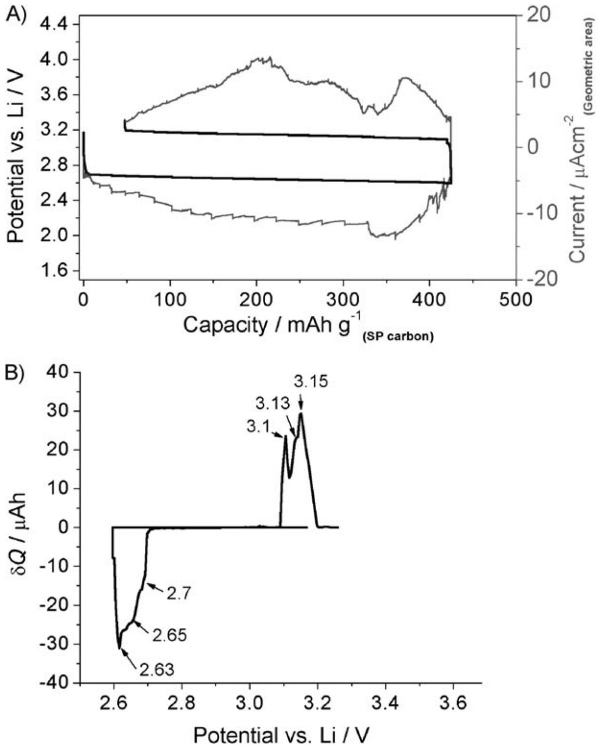


Figure 1. A) Potential (left) and current (right) versus the charge capacity normalized by the mass of the carbon and B) incremental charge (δQ) versus potential profiles of the potentiodynamic cycling with galvanostatic acceleration (PCGA) analysis performed on the cell with the configuration Li/PCE/SP-carbon,O_2.

In the reverse scan (oxidation process),[9] a sharp peak centered at 3.1 V versus Li, which should correspond to the reaction $2\,Li_2O \rightarrow Li_2O_2 + 2\,e^- + 2\,Li^+$ (or $2\,Li_2O \rightarrow 1/2\,Li_2O_2 + 1/2\,O_2 + 3\,e^- + 3\,Li^+$), is observed. The 3.1 V peak is followed by two overlapped peaks at potential values of 3.13 and 3.15 V versus Li, which can be associated with the reactions $Li_2O_2 \rightarrow LiO_2 + e^- + Li^+$ and $LiO_2 \rightarrow O_2 + e^- + Li^+$, respectively.

Under our low-current conditions, it was possible to clearly separate two reduction processes, probably from peroxide to oxide at the high potential (i.e., well above the cutoff voltage in conventional experiments) and to observe reversibility at 3.2 V versus Li^+/Li^0, that is, with a very low overvoltage with respect to the expected thermodynamic values. Note in Figure 1 A that the process evolves with a voltage gap at about 400 mV, which is the lowest reported to date in the absence of catalyst. Surprisingly, the gap (we report here the lowest at 400 mV, but more often it is quoted in the literature as at or above 1 V) between the first reduction and oxidation peaks has never been questioned and was generally attributed to the quasi-solubility of Li_2O_2, as no bond breaking or reconstruction takes place. In our case, using very low current and a high solvating medium resistant to deprotonation, there is no evidence of any residual current in this gap. The oxidation of H_2O_2 in water is known to give singlet O_2 ($1\Delta g$) which is approximately 1 eV more endothermic than triplet O_2 and is more or less rapidly deactivated in solution.[18] Arguably, singlet O_2 could also be formed from the oxidation of Li_2O_2, and the potential of 3.2 V would be a mixed potential between triplet (2.91 V) and singlet (ca. 3.9 V) forms of oxygen. This issues seems to have been overlooked by electrochemists. In the same vein, lithium equivalents of trioxidane H_2O_3*, not as discrete molecules but in the solid state or in clusters, that is $Li_2O + O_2 \rightleftharpoons \,<Li_2O_3^*>$, should be considered as possible intermediates which might be stabilized by the PEO-based composite electrolyte components (PEO, $CF_3SO_3^-$, and s-ZrO_2).[20]

To control the validity of our approach, we assembled a conventional cell, replacing the PEO-based solid electrolyte with a typical organic liquid electrolyte, that is, a solution of $LiPF_6$ in an ethylene carbonate/dimethyl carbonate (EC-DMC) solvent mixture, and carried out the same PGCA test performed in our solid-state cell. Figure 2 shows the results. Clearly, a quite different behavior, both in terms of kinetics and reversibility, is obtained. Figure 2 A, which illustrates the current–voltage trend, demonstrates a very poor reversibility (cf. Figure 1 A), while Figure 2 B, which illustrates the integrated PGCA response, reveals a high voltage separation between the peaks and a consistent reduction in charge balance (cf. Figure 1 B). These results confirm the difficulties in running the oxygen reduction process in cells using conventional, liquid organic carbonate electrolytes, as indeed reported by many authors.[1,14,15]

The reversibility of the redox process in our solid-state cell has been further studied by cyclic voltammetry at a scan rate of 100 $\mu V\,s^{-1}$. Figure 3 A reports the voltammetric profiles on a Li/PCE/SP-carbon,O_2 cell. In this case the peaks, previously observed without kinetic limits in the PCGA measurements, are shifted to lower (in reduction) and to higher (in oxidation)

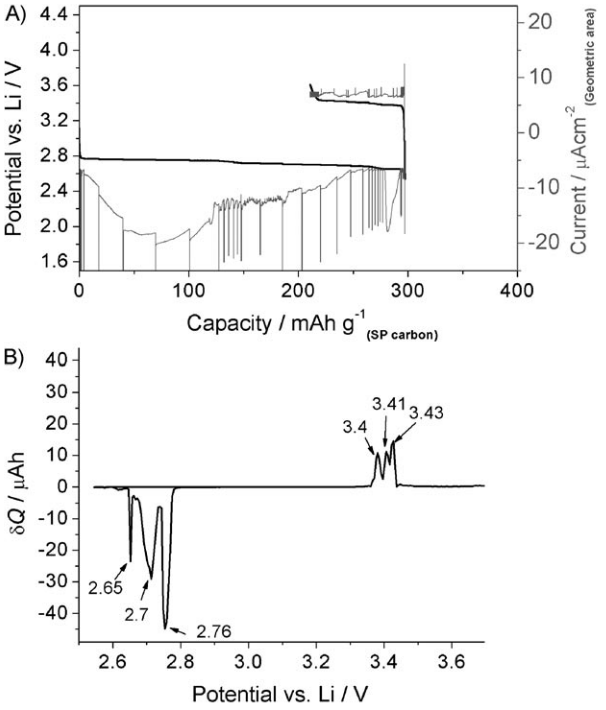


Figure 2. A) Potential (left) and current (right) versus the charge capacity normalized by the mass of the carbon and B) incremental charge (δ*Q*) versus potential profiles of the potentiodynamic cycling with galvanostatic acceleration (PCGA) analysis performed on a conventional cell having a Li/EC-DMC,$LiPF_6$/SP-carbon,O_2 configuration.

voltage values. The reduction peaks are merged into one single peak, while in oxidation two peaks are still observed. These trends of the voltammetric profiles are not surprising in view of the relatively high scan rate (particularly considering the solid polymeric system used for the cell assembly) and of possible kinetic limitations since only carbon, without catalyst addition, was used as our test electrode. Moreover, intrinsic limits associated with the electrode/electrolyte contact in this solid polymer cell configuration, reflecting high interphase resistance, cannot be excluded. A new electrode configuration, which contains a polymer binder different than poly(vinylidene fluoride) (PVdF) and is more compatible with the PEO electrolyte matrix, is a possible solution to overcome this drawback. Another improvement can be obtained by increasing the electrode porosity, which should lead to a larger electrode/electrolyte contact area. These aspects are under study and will be reported in the future.

The result of the CV test seems to confirm the reaction mechanism discussed on the basis of the PCGA results and clearly shows high reaction reversibility notwithstanding the peak separation of 400 mV. Furthermore, the photographs in Figure 3B, reporting the status of cell components after the CV runs, show that the electrodes (lithium and carbon) and the electrolyte (PCE) are still in excellent condition, thus confirming the protective role of the PEO matrix, in particular with respect to the metallic lithium electrode.

Finally, we complete our interpretation of the electrochemical process in the lithium–air cell by considering that oxidation of peroxides, including for example H_2O_2, proceeds

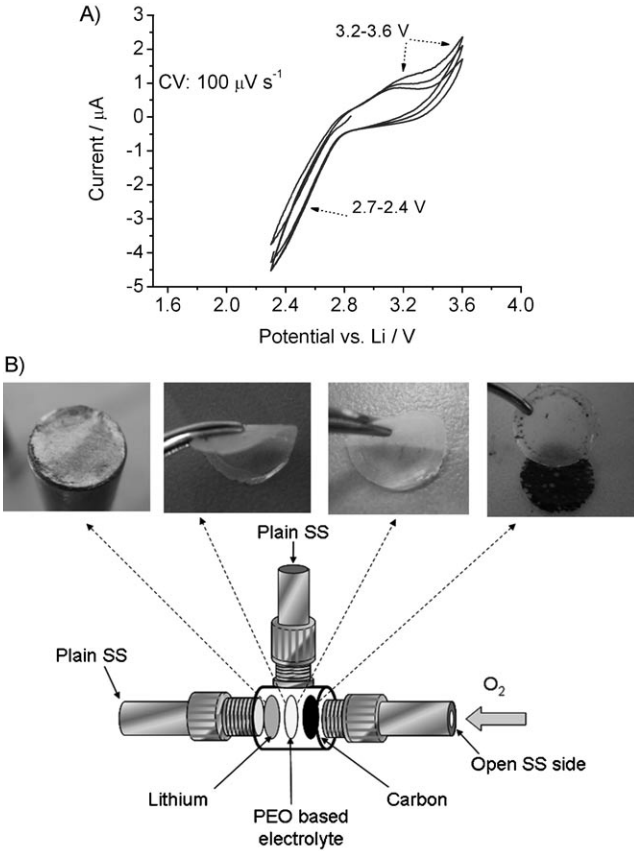
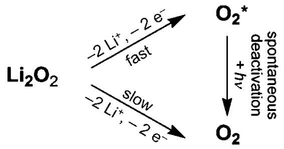


Figure 3. A) Cyclic voltammetry profiles at 100 $\mu V s^{-1}$ and B) schematic representation of the used T-cell and photographic images of the cell components after the cycling test of a Li/PCE/SP,O_2 cell. From left to right the photographic images show the lithium foil on the stainless steel (SS) piston, the PEO-based electrolyte membranes, and the SP carbon grid.

either rapidly to singlet oxygen, at a potential estimated at approximately +4 V versus Li^+/Li^0, or more slowly to triplet oxygen, the ground state at 3.1 V. The transition $O_2^* \rightarrow O_2$ is forbidden and thus slow. The potential observed in practice is a mixed potential between the two processes that depends on the lifetime of O_2^* in PEO and on the number of active collisions. For instance, the lifetime of O_2^* is 3 μs in water to about 700 μs in C_6D_6. These data suggest that additives (high atomic weight) could be added to the PEO to shorten the O_2^* time of existence. Formation of superoxide as an intermediate for the oxidation of peroxide is also possible, but is of only very marginal importance. This mechanism is shown schematically in Scheme 2.

The result reported herein demonstrate that the use of the very solvating, base-resistant PEO, plasticized by low-molecular-weight end-capped PEG, that is, tetraethylene glycol dimethyl ether, is a very good medium for the study of the electrochemistry of oxygen in water-free lithium–oxygen cells. We show that at low currents the perfect deconvolution of the peaks allows separation of at least two electrochemical processes attributed to peroxide and normal oxide. To our knowledge this is the first time that rechargeability with such a small peak separation is experimentally demonstrated. When larger currents are passed, the multiple peaks merge



Scheme 2. Proposed mechanism of lithium peroxide oxidation.

into a single wave, in each direction. The photographs of Figure 3B, reporting the status of the cell components after the CV runs, show that the electrodes (lithium and carbon) and the electrolyte (PCE) remain in excellent condition, thus demonstrating the protective role of the PEO matrix. These results, in addition to shedding light on the oxygen reaction mechanism in Li–air cells, confirm the practical feasibility of our solid-state concept, since the thin-film battery surfaces can be scaled up easily without concern for electrolyte leak or evaporation. Moreover, the presence of nanoparticles dispersed within the polymer electrolyte is expected to increase the convolution of O_2 diffusion, thus preventing self-discharge, a well-known fear in Li–air systems.

Another important side result of this study is the evidence that there is a "no-man's land" between 2.9 and 3.1 V versus Li^+:Li^0 in which no electrochemistry takes place; this gap leads to the hypothesis of singlet oxygen evolution. In this respect it has to be noted that even biological systems have not completely solved the problems of $O^{2-\cdot}$ during respiration and $(1\Delta g)$ oxygen evolution during photosynthesis. The simplest technique for testing this hypothesis could be the measurement of the red glow from O_2* deactivation. It also means that in practice, the cycle efficiency of a Li–air cell will not reach values greater than 87 % (our best case), as imposed by the mixed potential between singlet and triplet oxygen. This aspect must be considered when Li–air cells are envisioned for energy storage on a large scale, where practical 95 + % turnaround efficiencies are sought.

Experimental Section

Super P carbon electrode: The super P (SP) high-surface-area carbon electrode was fabricated in the form of a thin film by doctor-blade deposition of a slurry composed of 90 % SP and 10 % poly(vinylidene fluoride) (PVdF) 6020, Solvay Solef (binder) on a carbon-protected aluminum grid.

PEO-based electrolyte: The ZrO_2-added PEO-based polymer composite electrolyte (PCE) was prepared using poly(ethylene oxide) (PEO) (Aldrich; MW 6×10^5), nanoscale sulfonated ZrO_2 (Aldrich), and $LiCF_3SO_3$ (Aldrich) with a composition of $(PEO_{20}LiCF_3SO_3)$/s-ZrO_2 90:10 wt %, following a solvent-free procedure optimized in our laboratory, as described previously.[21] We made sure to have a uniform distribution of the ZrO_2 filler throughout the PCE membrane. This nanocomposite membrane showed a conductivity ranging between 10^{-4} and 10^{-5} S cm^{-1} at room temperature.

Cell prototypes: Three-arm T-cells, formed by a high-density polypropylene body in which three 10 mm diameter stainless steel plungers (acting as current collectors) were inserted and sealed with plastic front ferules (Figure 3B) were used for the electrochemical tests. The plunger facing the carbon electrode had been bored hollow to allow the oxygen flow that is contained in a latex rubber balloon statically connected to the plunger. Sandwiching a lithium metal foil anode, a PCE disc, and a SP grid cathode completed the cell.

Electrochemical measurements: The electrochemical characteristics of the cell were investigated by potentiodynamic cycling with galvanostatic acceleration (PCGA), which is a technique commonly exploited for characterization of electrochemical processes.[16–18] In our case, PCGA was performed by setting stepwise potential scans of 5 mV with a minimum current limit of 3–5 μA and a maximum single potential step duration of 3 h, using a Bistat Biologic-Science Instruments. The time integration of the current during each step gives the charge increment ($\delta Q = \int I_{(t)}\mathrm{d}t$). By repeating the experiment, we obtained a set of incremental charge values (δQ), which was plotted versus the applied potential.

Cyclic voltammetry, with a scan rate of 100 μV s^{-1}, was also performed in a 2.3–3.6 V voltage range using the Bistat Biologic-Science Instrument. All the data reported are representative of a series of reproducible results.

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