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Short communication

The SEI layer formed on lithium metal in the presence of oxygen: A seldom considered component in the development of the $Li–O_2$ battery

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HIGHLIGHTS

- ► The presence of O_2 influences the composition of the SEI on Li of the $Li–O_2$ battery.
- ► The SEI on Li anode of the $Li–O_2$ battery is unstable and changes during the cycling.
- ► $LiPF_6$ and PC decompose on the surface of the Li and contribute in formation of the SEI.
- ► Decomposed Kynar binder (degraded on the cathode) was observed on the surface of Li.
- ► Oxygen increases the resistance of the cells and influences the lithium stripping and plating.

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ABSTRACT

The SEI layer formed on metallic Li which has been used as an anode in a $Li–O_2$ battery is studied for the first time. We have used XPS to monitor the surface composition of the lithium electrode and have identified the various chemical species present. The XPS results indicated that the composition of the SEI layer is affected by the presence of oxygen and is unstable during cycling. We also observed decomposition products from the binder material used in the cathode on the surface of the lithium anode. This new SEI layer has an increased resistance affecting the lithium deposition which is essential for battery operation.

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1. Introduction

The demand for more advanced energy storage systems has grown in recent years and it is driven by the need for new electrified automotives. The lithium–oxygen battery is one candidate which could fulfil this increased demand due to the step change increase in specific energy it could potentially provide. However, several obstacles have now also become clear that hamper further progress [1]. During cycling of $Li–O_2$ batteries in non-aqueous electrolytes the oxygen reduction and oxidation evolution reactions (ORR and OER) take place in the pores of the carbon cathode during the discharge and charge respectively [2]. It has been shown that the ORR and OER result in the breakdown of not only the carbonate and ether based electrolytes [3–7] but also the salts such as $LiPF_6$, $LiB(CN)_4$, and LiBOB [6–8]. We have recently shown that the Kynar binder used for keeping the carbon cathode together also decomposes during the cycling of the $Li–O_2$ battery [7].

The mentioned studies [3–8] have focused solely on the degradation reactions occurring at the cathode of the battery with very little attention being placed on the stability of the Li anode or electrolytes in contact with Li anode in an oxygen atmosphere. Li metal is highly reactive, and in contact with non-aqueous liquids it is immediately covered by a passivation layer known as a solid electrolyte interphase (SEI) [9]. The SEI in alkyl carbonate based electrolytes has been widely attributed to the formation of lithium alkyl carbonate compounds ($ROCO_2Li$) and reduced electrolyte salts [10,11]. It has been shown that the thickness and the mass of the SEI on Li grows during cycling [12,13]. The chemistry and morphology has also been studied in the presence of trace amount of O_2 and H_2O in the electrolyte [14,15]. To the best of our knowledge all previous studies [10–16] of the SEI have focused on Li-ion batteries in a non-oxygen atmosphere.

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In this short communication we seek to discuss for the first time the surface layer on the Li anode in a Li–O_2 cell and highlight the possible effects on the lithium deposition and stripping reaction. Here we present a detailed surface characterization of the Li anode used in Li–O_2 cells that have been cycled in 1 atm of dry oxygen with a 1 M $LiPF_6$ in PC electrolyte. This was performed using X-ray photoelectron spectroscopy (XPS) on anodes removed from Li–O_2 batteries, after a single discharge, a single discharge followed by a single charged, and from a battery which had been stored. We also examined the deposition and stripping of Li on copper using cyclic voltammetry (CV) in cells kept in an oxygen or argon atmosphere.

2. Experimental

The Li–O_2 cells were assembled in an Argon filled glove box using the Swagelok design with the following components; lithium foil as anode, 1 M $LiPF_6$ in PC as the electrolyte, Solupor separator, and porous cathodes. The porous cathodes were made by mixing Super P carbon (Lithium battery grade, Erachem Comilog) with α-MnO_2 nanowire catalyst and Kynar 2801 (Arkema) binder using propylene carbonate (PC) (Ferro, Purolyte) and acetone as plasticizer and solvent. The weight ratio of carbon:catalyst:binder:PC was equal to 11:19:15:55, and the weight ratio of acetone:carbon was equal to 60–70 to 1. The α-MnO_2 nanowire catalyst was synthesized as described in reference [17]. The slurries were kept under magnetic stirring for about 4 h and then cast into an aluminium mesh. The cathodes were dried at 120 °C overnight in a vacuum furnace within an argon filled glove box before using in batteries. The Swagelok™ design was modified such that an opening allowed oxygen to access through the cathode. The cells were kept in home-made air-tight containers with inlet and outlet valves for oxygen gas purging. The containers were filled with a continuous flow of dry oxygen for about 2 h before starting discharge. A current density of 70 mA g^{-1} (gram of carbon in the cathode) was applied using a Digatron BTS-600 with lower and higher cut-off voltages of 2.6 and 3.9 V vs. Li, respectively. The three batteries were then exposed to the following conditions: “Stored”: kept in oxygen atmosphere for 2 days; “Discharged”: first discharge to 2.6 V; “Charged”: from freshly constructed discharged to 2.6 V and then charged to 3.9 V in constituting a single cycle. The current density of 70 mA g^{-1} was equal to ~0.025 mA cm^{-2} (area of the carbon electrode) for the “discharged” and “charged” cells, respectively. The discharge capacities of the cells were ~1.4 mAh cm^{-2}. The batteries were dismantled in an argon filled glove box and then, the Li anode was washed with a few drops of DMC prior to XPS characterization according to established procedures [18–20]. The effect of the washing procedure on the sample is still an open question for the experts in the XPS field. However, the general belief is that when an electrode is washed the XPS spectra originate from the SEI rather than from remaining salt and electrolyte solvent on the sample. Our several years’ experience in XPS measurements indicates that results from the washed samples are usually more reproducible. This procedure is also commonly used also by other groups [18–20].

To avoid contact with air the Li anodes were transferred from the glove box to the XPS analysis chamber within 15 min using a special built air-tight argon filled chamber. The XPS measurements were performed on a commercial PHI 5500 spectrometer, using monochromatized Al Kα radiation (1487 eV) and an electron emission angle of 45°. The dimensions of the probed region were approximately 2 × 4 mm. All spectra were energy calibrated by the hydrocarbon peak at the binding energy of 285.0 eV.

Electrochemical deposition and stripping of lithium was investigated in 2 identical Swagelok cells, however, the porous cathode was replaced by a copper grid (200 mesh). The cells were then sealed in an argon atmosphere or stored under a continuous flow of dry oxygen. The cells were kept for 14 h before any electrochemical measurement. Electrochemical impedance spectroscopy was then performed using a Bio-Logic SP240 instrument in frequency range was from 100 kHz to 0.1 Hz and the amplitude was 20 mV p–p. This was followed by cyclic voltammetry from open circuit voltage (~3 V vs. Li/Li^+) to −0.5 V followed by 10 cycles in the range −0.5 V to 1 V at scan rate of 100 mV s^{-1}.

3. Results and discussion

Our interest in the Li anode–electrolyte interface was initiated when we visually observed a black layer on the Li surface after disassembling several cycled Li–O_2 cells. This black layer appeared to become thicker during battery cycling and was unlike anything we had observed on the Li anodes of Li-ion batteries which had been cycled with similar current densities in the absence of O_2. In the following study we investigated the surface composition of this layer in presence of O_2.

The XPS survey scan (Fig. 1) of the surface of the stored, discharged and charged Li anodes showed the presence of only expected elements, i.e. C, O, Li, F, and P. This shows that no contaminants are present on the sample, and especially the lack of N 1s signal confirms that no air exposures of the samples occurred prior to XPS measurements, i.e. during the cycling or XPS preparation. The survey scan shows the variation in relative surface concentrations of each element between the three samples, and these are also summarized in Table 1. The Li surface of the stored sample in oxygen atmosphere shows much larger concentrations of carbon and oxygen than previously reported for Li stored in the absence of oxygen (a detailed comparison is given in Table 2 [11]). The second column in Table 2 shows the relative element surface composition of the stored samples (the Li anode of a Li–O_2 battery kept under oxygen atmosphere for 2 days), estimated using XPS assuming a uniform distribution of elements. The third column in Table 2 shows the relative element surface composition of Li metals immersed in 1 M $LiPF_6$ in PC electrolyte in an oxygen free atmosphere obtained from a publication by D. Aurbach et al. [11]. We can conclude that the relative amounts C and O are higher in the Li–O_2 sample rather than in the O_2 free sample, while the relative amount of Li and F is reduced in the presence of oxygen. This suggests that

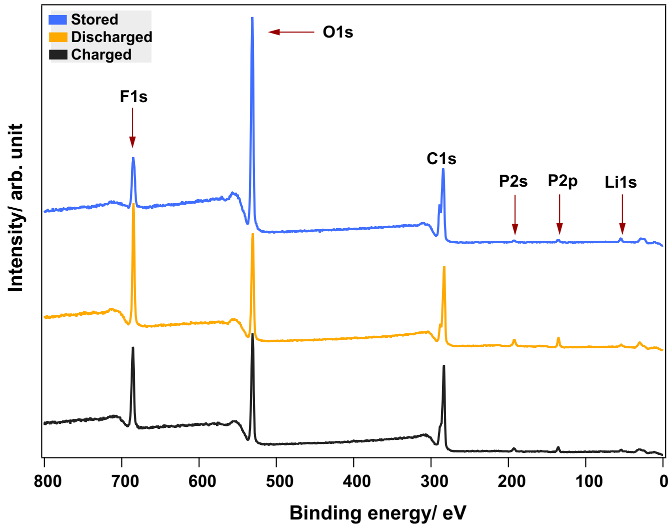

Fig. 1. Survey scan of Li anodes of the stored, discharged, and charged Li–O_2 cells containing 1 M $LiPF_6$ in PC.

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