



Scanning electrochemical microscopy of oxygen permeation through air-electrodes in lithium–air batteries



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ABSTRACT

Non-aqueous Li–air-batteries can provide potentially a very high energy density. The reaction at the positive electrode is the oxygen reduction reaction. Its products are lithium oxides (mainly Li_2O_2) that deposit as solid compound in the porous gas diffusion electrode (GDE). This can cause passivation of the electrode surface or clogging of gas diffusion pathway through the porous material. Here a new method is reported to measure in-situ the oxygen permeation through a GDE during the discharge process. It is based on the concepts of scanning electrochemical microscopy (SECM) in which a positionable microelectrode (ME) is used to detect the influx of oxygen in a deaerated electrolyte close to the outer surface of the GDE. However, no steady-state current for oxygen reduction at the ME can be obtained in Li-containing electrolytes because solid lithium oxides also deposit on the ME. Therefore, a pulsed potential program was developed that periodically removes deposits from the surface of the ME and eliminates the effect of surface passivation of the probe electrode. We validated this method by monitoring the oxygen reduction current at the ME as a result of oxygen permeating GDEs of different thickness.

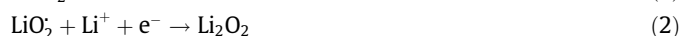
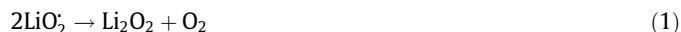
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1. Introduction

Since the first introduction of an aqueous Li–oxygen system by Galbraith [1] in 1976 a lot of efforts have been devoted to the development of a rechargeable Li–oxygen battery. Abraham et al. [2] reported on a non-aqueous Li–air cell, which raised hope for a readily available alternative to combustion propulsion systems due to its comparable high specific energy density of 3842 mA h g^{-1} [3]. However, substantial chemical as well as technical challenges have to be met to unleash the full potential of this energy storage technology. In the last decade, non-aqueous electrolytes have been investigated intensively because the spontaneous formation of a solid electrolyte interphase (SEI) in organic carbonates decelerates the corrosion of the Li electrode compared to aqueous electrolytes and allows exploiting the large cell voltages of more than 3 V. Nevertheless, no adequate aprotic electrolyte could have been found until now to sustain at the same time the hazardous environments of reactive oxygen species formed at the positive electrode and metallic lithium at the negative electrode. Alkyl carbonates for example decompose by nucleophilic attack of the superoxide [4]. It has been shown by quantum

mechanical calculations that sulfonate esters, aliphatic carboxylic esters, lactones, sulfones and alkyl esters of phosphinic, phosphonic and phosphoric acids are insufficient for the same reason [5].

At the positive electrode, molecular oxygen is expected to be reduced to the superoxide radical anion O_2^- which subsequently coordinates with Li^+ to form LiO_2 . Both radicals are highly reactive intermediates. The following conversion of LiO_2 to Li_2O_2 as final product can either happen by a chemical (Eq. (1)) or electrochemical (Eq. (2)) reactions [6].



The products of the oxygen reduction reaction (ORR) Li_2O_2 and Li_2O are not soluble in organic solvents and deposit as solids on the GDE leading to passivation of active sites within the electrode. Additionally, precipitates may clog the pores of the GDE. This limits the oxygen accessibility to the inner electrode surface and would result in capacity fading [7,8]. Measurements based on concepts taken from scanning electrochemical microscopy (SECM) [9] have already been used to characterize gas-evolving [10,11], gas-permeable [12], oxygen-evolution [13] or oxygen-consuming electrodes [14]. It has been demonstrated that O_2 and H_2O_2 can be detected in aqueous solution using the substrate-generation/tip collection (SG/TC) mode

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[10,15,16]. ORR activity has been characterized using the tip-generation/substrate collection mode [17] or the redox-competition mode [18]. Convective disturbance by rising gas bubbles has been counteracted by signal averaging over repeated identical experiments [10] or used as a source of additional information [19]. For a GDE in a Li–air battery one does not expect the occurrence of gas bubbles at least not during resting or discharge reaction. However, oxygen may transverse the gas–liquid interface within the pores of the GDE and diffuse into the electrolyte if it is not consumed completely in the discharge reaction. Positive electrodes in Li–air cells have been theoretically treated for diffusion-controlled reaction of oxygen inside pores [20]. Our method should provide excellent opportunities for spatial and temporal resolved measurements of the oxygen fluxes emerging from the GDE into the electrolyte at different states of charge if the discharge is interrupted. It is expected that such fluxes correlate with the degree of pore clogging.

However, a recent study of Gunasekara et al. [21] on ME diagnostics of Li–air batteries revealed a strikingly different behavior of oxygen reduction currents at a carbon ME in Li⁺-containing and Li⁺-free organic electrolytes. While the expected sigmoidal shape of cyclic voltammograms (CVs) was found for electrolytes with tetrabutylammonium (TBA⁺) salts, the presence of Li⁺ lead to distorted CVs. After reaching the maximum current, the signal decreased rapidly at more negative potentials. They conclude that this behavior does not arise from oxygen mass transport limitations towards the ME, since a steady-state ORR current was observed in TBA⁺-containing solution, but from passivation of the ME by the non-soluble ORR products. Quantifying the extent of passivation revealed that it is insufficient to be the only explanation. Gunasekara et al. [21] further conclude that a combination of passivation and repulsion of the initial ORR product O₂^{•−} causes the current decay.

To our judgment, the procedure by Gunasekara et al. [21] does not seem feasible for long term observation in Li ion-containing electrolytes due to the fact that no steady-state current can be reached. Based on the re-investigation of fading ORR reduction current at Pt ME in Li⁺-containing organic electrolytes, a new pulse program is proposed that avoids the passivation of the MEs and allowed a quantitative determination of local oxygen ingress through GDEs in such electrolytes.

2. Material and methods

2.1. Chemicals

The dimethyl sulfoxide (DMSO, 98% purity, Carl Roth GmbH, Karlsruhe, Germany) was deaerated and dried for at least 48 h over a 3 Å molar sieve. Solutions from 0.1 M tetrabutylammonium perchlorate (TBAClO₄, purity ≥ 99%, Sigma–Aldrich, Munich, Germany) in dried DMSO and 1 M LiClO₄ in dried DMSO were prepared inside a Ar-filled glovebox. The electrolyte was transferred to the SECM via a syringe.

2.2. Electrodes

The electrochemical four-electrode cell consisted of a Pt ME with 20 μm diameter, a GDE as working electrodes (WEs), a platinum wire as auxiliary electrode and a silver wire as quasi-reference electrode (AgQRE). All potentials are quoted with respect to the AgQRE. The Pt MEs were produced by sealing a Pt wire with the laser-based micropipette puller system P-2000 (Sutter Instruments, Novato, USA). The *RG*-value describing the ratio of outer probe diameter and the diameter of the electrochemically active area was determined to be 6. The ME was successively polished

in an aqueous suspension of 0.3 μm and 0.05 μm Al₂O₃ particles (MicroPolish II, Buehler, Düsseldorf, Germany).

The two-layer GDE consisted of a gas diffusion layer (GDL) placed on carbon paper (Toray™ TP060, Toray Industries, Inc., Tokyo, Japan). To prepare the GDL, carbon particles (Vulcan XC R, Worlee-Chemie GmbH, Hamburg, Germany) and binder (Kynar Flex 2801, Tetrachim, Noisiel, France) were uniformly dispersed in N-ethylpyrrolidone (Carl Roth GmbH + Co. KG., Karlsruhe, Germany). The carbon paper was hydrophobized by immersion into a polytetrafluoroethylene suspension (polytetrafluoroethylene preparation, 60 wt.% in H₂O, Sigma–Aldrich, Munich, Germany) for 30 s in order to prevent that the solvent can wet this layer. A slurry of Vulcan XC R was applied on top of the carbon paper by a doctor blade (Werner Mathis AG, Oberhasli, Switzerland). Finally the GDE was dried in a two-step process (30 min at 80 °C followed by 90 min at 120 °C). Electrodes of different thickness were prepared.

2.3. Experimental setup

All experiments were carried out in an in-house developed SECM-setup (Fig. 1). It is adapted from an earlier design [22] amended by a second gas reservoir below the sample. This allowed establishing concentration gradients across the GDE (used as sample in Figs. 6 and 7) by connecting the separate gas inlets to different gas sources. A defined Ar/O₂ gas mixture was obtained by mixing high purity Ar and O₂ using two mass flow meters (F-201CV-020 and F-201CV-050, Bronkhorst, Netherlands). The gas mixture was purged continuously into the lower gas reservoir while the upper gas reservoir was purged with pure Ar. A septum in the upper gas reservoir was used to inject deaerated electrolyte solutions into the liquid reservoir within the Ar-filled gas reservoir. This procedure dramatically shortened the time for obtaining an oxygen free solution within the measurement head compared to our previous designs. The PTFE cell, platinum and silver wires were sonicated in acetone, ethanol and deionized water for 3 min respectively followed by drying in an argon stream. In addition the PTFE cell was dried for 30 min at 120 °C in an oven. The GDE was mounted with the hydrophobic carbon paper facing the lower gas chamber. Due to the fragility of the GDE, the carbon paper was glued to the conductor disc (part 5 in Fig. 1) in using polydimethylsiloxane (PDMS, base and curing agent of SYLGARD184

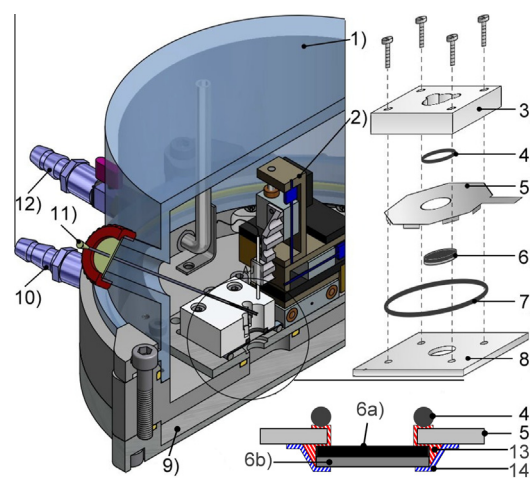


Fig. 1. Cross sectional view of SECM setup: (1) upper chamber, (2) piezo motors, (3) PTFE liquid reservoir, (4) O-ring, (5) conductive sheet, (6) GDE (sample), (6a) GDL, (6b) PTFE treated Toray paper, (7) O-ring, (8) base plate, (9) lower gas reservoir, (10) gas inlet for lower gas reservoir, (11) needle for injecting electrolyte solution, (12) gas inlet for upper gas reservoir, (13) PDMS, and (14) silver varnish.

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