

Factors affecting the electrochemical performances of lithium-air cells in tetraglyme based electrolytes

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Nowadays, intensive research is focused on alternative battery systems that can provide a breakthrough in terms of energy density as compared to Li-ion batteries [1]. Among such battery systems, Li-air battery system is considered by many to represent the holy grail of batteries [2]. Such consideration, in particular, is based on the fact that the positive active material (i.e. oxygen) is not stored inside the battery but is, externally, supplied during the battery operation. In this way, the energy density calculated for a non-aqueous Li-air system reaches a theoretical value of 11.4 kWh/kg (neglecting the mass of oxygen) and around 5.2 kWh/kg including the weight of the oxygen, respectively [3, 4].

The positive electrode of the Li-air battery is more characteristic to fuel-cell technology rather to the secondary Li-ion battery. The electrode (i.e. the gas diffusion electrode, or GDE), in its simplest form, contains a porous carbon that is additionally mixed with a fluorinated binder for good mechanical properties. The electrochemical reaction during discharge process in non-aqueous electrolytes, involves the reduction of the active material to a series of intermediates. Further, these intermediates convert to the oxygen reduction reaction (ORR) main products Li_2O_2 and Li_2O [5]. Due to its reversibility during the oxygen evolution reaction (OER), Li_2O_2 represents the desired product of the oxygen reduction in Li-air cells. To improve the energetic efficiency of the two reactions, it is a common sense that the carbon of the GDE contains additionally an electrocatalyst [6].

The electrochemical performances of the Li-air battery are governed by the stability of the cell components in the presence of the oxygen reaction intermediates and products [7-9]. Moreover, it seems that each cell component in part has its own contribution to the final electrochemical performances of the Li-air cell. At the positive part of the cell, the consumption of the ORR intermediates in side reactions decrease the amount of Li_2O_2 that is forming. Furthermore, the negative part of the Li-air cell, i.e. metallic lithium, consumes already the electrolyte during the solid-electrolyte interphase (SEI) formation, even before the cycling of the cell has started.

Our investigations on Li-air cells with tetraglyme based electrolytes indicate that the product of the oxygen reduction is indeed Li_2O_2 (Figure 1). No additional reflections (Li_2CO_3) were identified in the XRD pattern of the electrode discharged at 2V except the LiOH reflections which could arise from the long exposure of the sample to moisture from air; nevertheless, reducing the air exposure no LiOH reflections were visible. The Li-air cell impedance (Figure 2) is affected by the processes that occur at the cathode side during the cell operation

(i.e. formation of Li_2O_2) and at the anode side during the cell calendaring (e.g. growth of the SEI at the metal electrode). In this study, we investigate the performance evolution of the Li-air cells during continuous discharge-charge reactions. In particular, the work will be focused on the behavior of the cell components in the presence of both the tetraglyme based electrolytes and oxygen reduction intermediates and products.

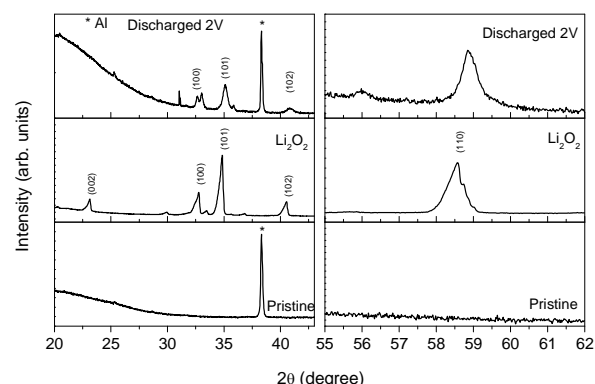


Figure 1. Comparison between the XRD patterns of the pristine electrode (bottom), pristine Li_2O_2 (middle) with the oxygen electrode discharged to 2V (top) during the first cycle.

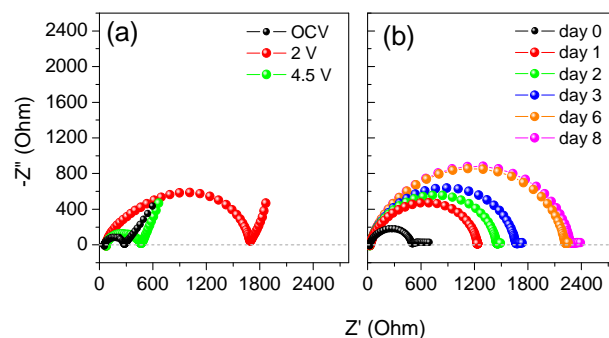


Figure 2. Nyquist plot evolution of (a) an oxygen electrode during cycling and (b) a symmetric Li-Li cell during calendaring. Electrolyte: 1M LiPF_6 in TEG-DME.

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