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Distribution of discharge products inside of the lithium/oxygen battery cathode

Ingo Bardenhagen [a, b, *], Mandus Fenske [a], Daniela Fenske [a], Arne Wittstock [b], Marcus Bäumer [b]

[a] Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Str. 12, 28359 Bremen, Germany
[b] Institute for Applied and Physical Chemistry and Center for Environmental Research and Sustainable Technology, University Bremen, Leobener Str. UFT, 28359 Bremen, Germany

HIGHLIGHTS

- Homogeneous discharge product deposition in macropores.
- Restricted oxygen diffusion limits the discharge product formation in mesopores.
- Direct oxygen feed enhances the lithium carbonate and lithium oxide formation.
- LiF forms during the discharge reaction due to electrolyte and binder degradation.

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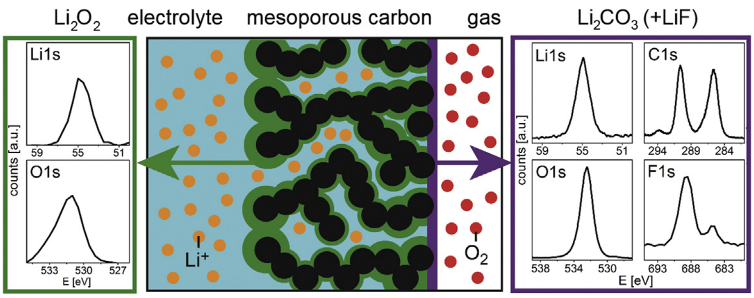
GRAPHICAL ABSTRACT



ABSTRACT

During the discharge of an aprotic Li/O_2 battery solid products assemble inside of the gas diffusion electrodes (GDE). The distribution of these in dependence of pore size of the GDE is investigated by X-ray Photoelectron Spectroscopy (XPS). Depth profiling of the electrolyte facing side of the cathode reveal that macroporous electrodes are able to store discharge products homogeneously in the pore structure. Mesoporous GDE, however, develop a concentration gradient with large amounts of discharge product at the electrode/electrolyte interface and low amount in the bulk of the electrode. The investigation of the cross-section of these GDE reveals that most of the discharge products form near the oxygen facing side of the GDE. Here, the chemical compositions differ strongly from those at the electrolyte facing side. The high oxygen concentration and the limited lithium supply lead to the formation of lithium carbonate, lithium oxide and lithium fluoride. Also a thin layer of discharge product blocking further oxygen supply into the GDE through macroporous cracks is formed at the gas/electrolyte interface.

1. Introduction

The development of electrochemical power sources with high gravimetric energy is driven by the large energy consumption of mobile electric devices. Especially fully electric vehicles have a need for these kind of batteries to allow driving ranges competitive to cars with combustion engines. The aprotic Li/O_2 battery has the

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* Corresponding author. Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Wiener Str. 12, 28359 Bremen, Germany.

E-mail addresses: ingo.bardenhagen@ifam.fraunhofer.de (I. Bardenhagen), mandus.fenske@ifam.fraunhofer.de (M. Fenske), daniela.fenske@ifam.fraunhofer.de (D. Fenske), awittstock@uni-bremen.de (A. Wittstock), mbaeumer@uni-bremen.de (M. Bäumer).

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potential to deliver up to 3505 Whkg^{-1}, which is nearly ten times higher than that of the conventional lithium ion battery [1]. In this type of battery, the desired reversible reaction is the reduction of molecular oxygen which reacts with lithium ions to solid lithium peroxide ($O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$). This reaction is believed to consist of two steps: the one electron reduction of oxygen to form lithium superoxide (LiO_2) which disproportionates in a second process to the peroxide and molecular oxygen. In the battery, this part of the discharge reaction occurs at the cathode which is a gas diffusion electrode (GDE) while the anode delivers lithium ions and ideally consists of metallic lithium ($Li \rightarrow Li^+ + e^-$). To achieve the theoretical energy density the GDE needs to be completely and homogeneously filled by Li_2O_2. Critical factors are pore size and volume inside of the active material of the GDE and the wetting of the pores with electrolyte [2,3]. However, due to the deposition of the discharge product in the GDE some challenges arise:

(1) The Li_2O_2 is insulating and hinders the required electron transfer from the cathode to the molecular oxygen [4].
(2) The deposition of Li_2O_2 will narrow the pores in the GDE which will hinder oxygen diffusion and Li ion movement [5].
(3) In case of mesoporous electrodes the pore narrowing can also lead to clogging preventing further oxygen supply [6,7].

The deposition of discharge product is mostly investigated by scanning electron microscopy (SEM), Infrared Spectroscopy (IR), X-Ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of the electrolyte facing side of the GDE. It has been shown that the discharge current influences the Li_2O_2 precipitate where low currents lead to toroidal aggregates and high currents lead to films on the carbon substrate [8–14]. The question how the discharge product forms in the bulk of the active material of the GDE is still open.

One method to look into deeper layers of the discharged GDE is the depth profiling. Here, the electrolyte facing surface of the electrode is subsequently etched with argon ions and measured by XPS. The relative amount of each element can be calculated from the recorded spectra and give an insight into the homogeneity of the discharge product deposition. This technique has been applied by several groups to study the SEI on Li [15–18] and on carbonaceous materials [19,20] in different solvents as well as for catalyst and microporous layers of a fuel cell [21,22].

Besides the homogeneity the XPS measurements also allows for a characterization of the chemical state of the discharge products. Due to the high chemical reactivity of the lithium oxygen species in the cell different non-rechargeable side products may appear. First, the lithium peroxide may be further reduced to the thermodynamically stable lithium oxide (Eq. (1)) [1]. In addition, the peroxide or its predecessor the superoxide may also react with the passive parts of the cell, namely the electrolyte and the GDE itself, to form either lithium carbonate (Eq. (2)) or lithium fluoride (Eq. (3)) [9,23]. All three side products are formed irreversible and thereby lower the rechargeability and the capacity of the Li/O_2 battery.

$$Li_2O_2 + Li^+ + e^- \rightarrow 2\ Li_2O \tag{1}$$

$$Li_2O_2 + C + \frac{1}{2}O_2 \rightarrow Li_2CO_3 \tag{2}$$

$$LiO_{2(s)} + -(CH_2 - CF_2)-_{(s)} \rightarrow HO_2 + -(CH{=}CF)-_{(s)} + LiF_{(s)} \tag{3}$$

In this work the type of discharge product and the deposition in the bulk of the GDE in dependence of its porosity is investigated by XPS. A commercial macroporous Freudenberg H2315 C2 GDE and a mesoporous carbon xerogel GDE were discharged in a Li/O_2 cell prior to the XPS measurements. Besides the GDE as cathode, the cell consisted of a lithium metal anode and 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in dimethyl sulfoxide (DMSO) as electrolyte. Despite its limited long term stability owing to reactions with the lithium metal [24] DMSO performs well in stabilizing the superoxide radical [25,26]. For both kind of GDE depth profiles were recorded starting from the electrolyte-facing side. Also cross-sectional XPS of the 150 μm thick xerogel electrode was used to gain further insight into the deposition of discharge product in mesoporous carbon materials. The chemical composition of the discharge product at the oxygen-facing side of the xerogel GDE was measured to reveal the reactions at the gas/liquid interface.

Prior to the discharged electrodes a benchmark electrode was prepared to evaluate the influence of the argon-ion sputtering on the results of the XPS measurements. Here, Li_2CO_3 was mixed in a carbon matrix as reference discharge product which is believed to stay unchanged during the preparation process due to its high chemical stability.

2. Experimental

The production of the carbon fiber-supported xerogel electrode is described in detail elsewhere [6]. Briefly, carbon fiber paper (Toray Paper TGP-060) was pretreated with an oxygen plasma (5 min, 50 W) inside a plasma chamber (Oxford Instruments, PlasmalabSystem100) to increase the hydrophilicity. The etched papers were cut into discs with a diameter of 10 mm and then impregnated with an aqueous sol consisting of resorcinol, formaldehyde and sodium carbonate as catalyst. After curing for 3 days at 353 K the gelated samples were rinsed with acetone and air-dried before pyrolysis in a tubular furnace purged with Ar. The furnace was first heated to 473 K at 5.8 K min^{-1} and kept at 423 K for 30 min. Then it was further heated to 1073 K at 10 K min^{-1} and held for 60 min before cooling down to room temperature.

The benchmark sample for the sputter experiments was made by mixing 50 w% carbon black (Vulcan® XC72R) and 30 w% Li_2CO_3 (Sigma Aldrich) together with 20 w% PVDF Binder (Kynar®) in N-Ethylpyrrolidone (Carl Roth) to form a slurry. After casting on a copper foil the layer was dried for 1 h at room temperature prior to a two-step drying procedure for 30 min at 353 K and for 90 min at 393 K.

SEM was employed to investigate the surface and the cross-section of the two electrodes before discharge and the deposits at the oxygen facing side of the xerogel GDE after discharge. The high resolution surface images were carried out using a FE-SEM Leo 1530 Gemini instrument (Carl Zeiss SMT GmbH, Oberkochen, Germany) and the cross-section images using a Phenom ProX Desktop instrument (Phenom-World BV, Eindhoven, Netherlands). To determine the porosity of the xerogel GDE nitrogen adsorption experiments were conducted employing a Nova 2000E (Quantachrome Instrument Corp., Boynton Beach, Florida, USA). The Barrett–Joyner–Halenda (BJH) method was used to determine the mean pore diameter.

The galvanostatic discharge of the GDE was conducted with a Solartron 1470E potentiostat (AMETEK Inc., Berwyn, Pennsylvania, USA) at 0.1 mA cm^{-2} under 2 bar oxygen pressure and a cut-off voltage of 2.6 V. The battery setup has been described previously [6]. It consists of a metallic lithium as anode, the GDE as cathode and a filter paper (Whatman® Grade 1) soaked with 50 μL 1 M LiTFSI in dimethyl sulfoxide (DMSO) electrolyte. After the measurement the cells were disassembled in an argon filled glove box to avoid reaction with water or CO_2 from ambient air. The GDE were