

# Materials for Energy Technology

## MS.4.085

### Electron microscopic and electrochemical characterization of Li-air battery materials

S. Eswara Moorthy<sup>1</sup>, M. Marinaro<sup>2</sup>, J. Bernhard<sup>1</sup>, J. Biskupek<sup>1</sup>, D. Geiger<sup>1</sup>, L. Jörissen<sup>2</sup>, M. Wohlfahrt-Mehrens<sup>2</sup>, U. Kaiser<sup>1</sup>

<sup>1</sup>Electron Microscopy Group of Materials Science, University of Ulm, 89081 Ulm, Germany, Germany

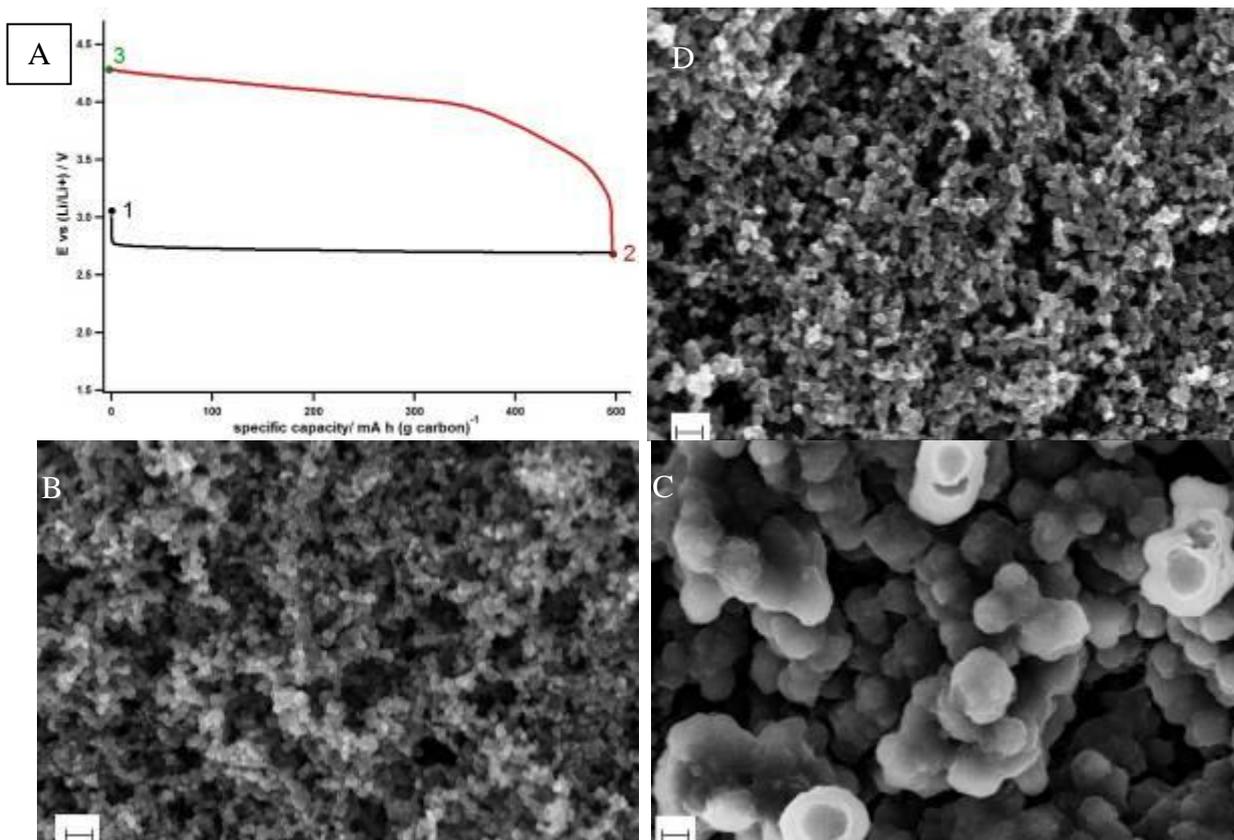
<sup>2</sup>Centre for Solar Energy and Hydrogen Research BW, 89081 Ulm, Germany, Germany

santhana.eswara@uni-ulm.de

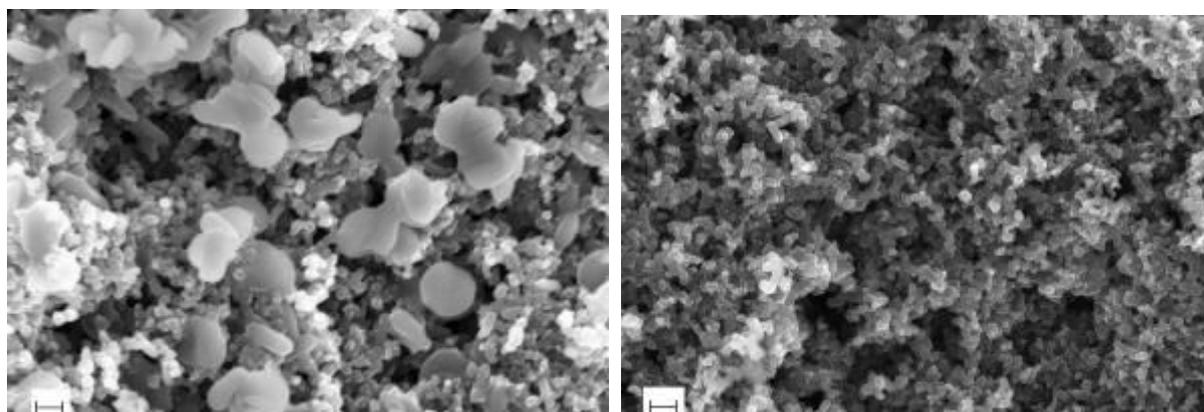
Keywords: Li-air battery, TEM, pore structure

Lithium-based batteries are one of the most important groups of rechargeable batteries in portable electronic devices owing to their high gravimetric energy-density. An increasing scientific and technological interest in further improving the energy-capacity and the number of charge-discharge cycles has provided significant impetus for further innovations in the field of Li-Air batteries [1, 2]. However, one of the most severe limitations in the commercialization of the Li-Air batteries is that the oxygen reduction reaction (ORR) during discharging and oxygen evolution reaction (OER) during charging must have fast kinetics. In order to enhance the ORR and OER reaction kinetics and to suppress any parasitic reactions, innovations in developing suitable electrocatalysts as well as suitable characterization techniques are necessary. In the current work, we employed electron microscopy (TEM and SEM) as well as Focused Ion Beam (FIB) techniques to characterize the reaction products and the electrocatalysts in order to gain a deeper understanding of the underlying reactions and their mechanisms to improve reaction efficiencies. The SEM images of the gas diffusion electrode at pristine, discharged and recharged states and corresponding galvanostatic curve (up to 500 mA.h/(g carbon)) are shown in Figure 1. Discharging the battery forms lithium peroxide on the cathode. Upon recharge, it disappears. Our SEM results are consistent with XRD results which show  $\text{Li}_2\text{O}_2$  peaks in discharged case but not in recharged case. These results are also consistent with Electrochemical Impedance Spectroscopy results. Another set of electrodes, in this case discharged up to 1000 mA.h/(g carbon) were also investigated. These results are shown in Figure 2. Formation and dissolution of lithium peroxide upon discharging and recharging are evident from these figures. The size of the lithium peroxide crystals are in the range of 250-350 nm and the morphology is rather smooth. Determination of the pore structures and tortuosity [3] in the gas diffusion electrode is important to design and develop an optimal electrode structure to facilitate the oxidation and reduction kinetics. In order to obtain the 3-D morphology of the pores in the electrode, FIB tomography methods were employed. Our first results showed that sufficient contrast between the carbon electrode and the background is indispensable for the reconstruction of the pores. Therefore, the discharged and recharged electrodes were vacuum-impregnated with commercial epoxy. Furthermore, we are characterizing numerous candidates for bifunctional electrocatalysts. There are two major classes of electrocatalysts viz., noble metal based and oxide based, that are being investigated. In our contribution, we will share our latest results from this on-going research work on mechanistic understanding of electrochemical reaction products and optimized imaging conditions.

1. M. Armand and J.-M. Tarascone, *Nature*, (2008), 451, 652-657
2. J. Christensen et al, *J. Electrochem. Soc.*, 159(2), (2012), R1-R30
3. M. Ender, J. Joos, T. Carraro and E. Ivers-Tiffée, *J. Electrochemical society*, 159(7), A972-A980 (2012)
4. The authors gratefully acknowledge funding from the German Federal Ministry of Education and Research (BMBF) under the project 'Strom aus Luft und Li'.



**Figure 1.** The galvanostatic discharge/charge curve (A) and microstructures of pristine (B), discharged (C) and recharged (D) electrodes. The scale bars correspond to 200 nm.



**Figure 2.** Microstructure of the discharged (left) and recharged (right) electrodes. The formation of lithium peroxide crystals on the discharged electrode (up to 1000 mA.h/ g carbon) in the form of large crystals with smooth morphologies are clearly visible. The scale bars correspond to 200 nm.