Post Li-Ion Batteries

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In the last decades, the investigation of new secondary cells has been increased considerably. Very promising battery systems are the so called "Post Li-ion batteries" with metal anodes: metal-sulfur and metal-air (oxygen) batteries, in particular Li-sulfur, Mg-sulfur, Zn-air and Li-air batteries.

Li-sulfur battery is a promising system, due to its high theoretical capacity (1675 mAh/g_{sulfur}), energy density (2500 Wh/kg), the low cost and non-toxicity of sulfur. Nevertheless, some of the drawbacks of lithium-sulfur batteries are the poor rechargeability and high self-discharge rates. Due to the low electrical conductivity of sulfur, electrical conductive material has to be added in order to encourage the electrochemical reaction. Furthermore, polysulfides of high order (Li₂Sn with $2 \le n \le 8$) dissolve in the electrolyte and can diffuse to the anode and react directly with lithium metal. This so-called shuttle mechanism causes irreversible loss of sulfur.

Carbon aerogels are a highly promising material to be used as matrix for sulfur to fabricate cathode for lithium-sulfur batteries. Resulting from organic resorcinol-formaldehyde aerogels, carbon aerogels exhibit highly porous structure with porosity up to 97%, high surface area about 500-3500 m²·g-1, large pore volume about 2-3 cm³·g⁻¹, and good electronic conductivity. Additionally, the important advantage of carbon aerogel is its tunable porous structure and pore size distribution. In the presentation actual results will be discussed.

Zinc based **metal-air** batteries have the advantage of high energy density, because oxygen from ambient air is used without in-cell storage. As a consequence, lighter batteries are produced with the reversible available Zinc as the only limiting factor.

However, before Zn-air batteries can be used as secondary elements some obstacles have to be overcome. The low cyclability of state of the art Zn-air batteries is caused by the passivation rate and dendrite growth of zinc, carbonate formation in the alkaline electrolytes, corrosion of cathode materials and flooding of the cathode.

The flooding of the cathode has different origins; one is the increase of electrolyte pressure inside the cell, due to the volume expansion of the zinc anode. To mimic this behavior, different hydrostatic pressures from 5.2 mbar to 26 mbar were applied during measurement of the polarization curves and electrochemical impedance spectra (EIS).

Bifunctional Ni/Co₃O₄ based electrodes [1, 2] were produced by the RMR technique [3] and the porous structure was varied by applying different pressures (4 bar, 6 bar and 10 bar) during production of the electrodes by hydraulic hot pressing. These electrodes were used to investigate how the electrolyte penetration depth influences the

electrochemical performance and how this behavior can be influenced by the porous electrode structure.

The electrochemical measurements during oxygen reduction reaction (battery discharging mode) were performed in a 7.5 M KOH solution, at 25°C with neat oxygen using a homemade hydrostatic half-cell, a RHE reference electrode (Hydroflex from Gaskatel, Germany) and a Pt counter electrode. Electrochemical impedance spectra (Figure 1) were recorded at different current densities in the frequency range from 20 mHz to 100 kHz.

The equivalent circuit used for the evaluation of the measured spectra consists of a series combination of charge transfer resistance and diffusion impedance element (Nernst impedance) in parallel to the double layer capacity imbedded in the porous electrode model of Göhr and in series with the electrolyte resistance and inductance from wiring.



Figure 1: Nyquist representation (a) and Bode representation (b) of EIS measured during ORR of electrode produced at 4 bar, hydrostatic electrolyte pressure 4 mbar at different current densities

References

[1] D. Wittmaier, T. Danner, N. Wagner, K.A. Friedrich, Screening and further investigations on promising bi-functional catalysts for metal-air batteries with an aqueous alkaline electrolyte, Journal of Applied Electrochemistry, 44 (2014) 73-85

[2] D. Wittmaier, S. Aisenbrey, N. Wagner, K. A. Friedrich, Carbon-free nickel-cobalt oxide cathodes for lithium-air batteries with an aqueous alkaline electrolyte, Electrochim. Acta, 149 (2014) 355-363

[3] E. Gülzow, N. Wagner, M. Schulze, Preparation of gas diffusion electrodes with silver catalysts for alkaline fuel cells, Fuel Cells – From Fundamentals to Systems, 3 (2003) 67-72

[4] N. Wagner, "Electrochemical power sources – Fuel cells" in Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd Edition, Edited by Evgenij Barsoukov and J. Ross Macdonald, John Wiley&Sons, Inc., ISBN: 0-471-64749-7, pp.497-537, 2005