Abstract #983, 224th ECS Meeting, © 2013 The Electrochemical Society

Analysis of the Manganese Dissolution and Deposition in $LiMn_2O_4/Li_4Ti_5O_{12}$ based Lithium-Ion Batteries

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$LiMn_2O_4$ (LMO) has been studied extensively over the last few years as it is one of the most promising cathode materials for the use in commercial lithium-ion batteries. Apart from its high potential of 4 V vs. Li/Li^+ its benefits are the low costs and the environmental benignity compared to other cathode materials containing for example cobalt or nickel. However it suffers from capacity fading during cycling due to the dissolution of manganese into the electrolyte.

Several research groups investigated this fading mechanism and ascribed the dissolution of the active material mainly to the Jahn-Teller distortion [1] and the disproportion reaction [2]. Whereas the repeated onset and relaxation of the Jahn-Teller distortion leads to structural damage and the loss of active material [1], the disproportion reaction is an acidic-induced degradation on the surface of the active material [3]. Various theoretical and experimental approaches have been reported to investigate the dependence of the manganese dissolution on the charge/discharge rate and the temperature. However most experiments included a modified cell setup that potentially affected the chemical processes within the cell. [1, 4] Furthermore it was reported that the dissolved manganese ions destructively interact with the solid electrolyte interface (SEI) on carbonaceous anodes. [5] Therefore the most suitable approach to examine the manganese dissolution in a full cell was found to be the use of a $Li_4Ti_5O_{12}$ (LTO) anode material. With its potential of 1.5 V vs. Li/Li^+ it does not feature the formation of a SEI compared to carbonaceous anodes. Thus the manganese dissolution was investigated by analyzing the deposition of the dissolved manganese ions on a LTO anode.

The dissolved manganese ions migrate to the anode and do not form a surface layer but discrete particles as shown in Fig. 1. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) revealed the particles to consist of manganese and oxygen. EDX mappings of larger areas of the sample showed that manganese oxide particles grow at several spots on the LTO anode. Further investigations were performed to determine the structure and composition of the manganese oxide particles including Raman spectroscopy and Laser ablation mapping experiments coupled with inductively coupled plasma mass spectrometry (ICP-MS). The Raman spectrum of the particles features different bands that can be attributed to manganese oxide vibration modes and besides clearly deviate from the LTO spectrum. Potential manganese oxide compositions were analyzed by Raman spectroscopy to determine the exact composition of the deposited manganese oxide particles.

Fig. 1: SEM image of a manganese oxide particle on a LTO anode.

In this study the manganese dissolution was investigated in 40 Ah cells that were designed for the use in an electric vehicle. To examine the rate dependence of this fading effect, the cells were cycled with two different charge/discharge rates (1C, 2C) and a driving cycle that simulated the use of the cell in an electric vehicle. Furthermore the cycling took place at three temperatures including 23°C, 35°C and 45°C. The comparison of the EDX mappings of the samples cycled with different rates and temperatures suggest general tendencies concerning the quantity and size of the manganese oxide particles. Regarding the small section of the electrode surface covered by EDX measurements, the rate and temperature dependence of particle size and quantity had to be confirmed by further experiments. Therefore Raman mappings were performed to examine the temperature dependence of the amount of deposited manganese oxide particles. However, since SEM, EDX and Raman spectroscopy are very surface sensitive, the measurements do not give information about the actual amount of deposited manganese oxide. Thus flat particles and tower-shaped particles with the same cross section would yield the same result. The analysis of the amount of deposited manganese was accomplished by Laser ablation measurements coupled with ICP-MS. These Laser ablation mapping experiments clarified the charge/discharge rate dependence of the manganese dissolution at the LMO cathode as well as the deposition behavior at the LTO anode. Moreover three-dimensional SEM measurements were performed to further investigate the nature of the manganese deposition on the LTO anode. The shape and height of the manganese particles correlate with the assumptions made for the Laser ablation measurements.

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