Electrochemical Activity of Solvothermally Treated Electrochemical MnO_2

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Electrochemical manganese dioxide (EMD) is one of the most popular cathode materials for primary batteries. One of the major drawbacks of the EMD when used in aqueous batteries is significant difference between theoretical and practically attainable specific capacity. The theoretical capacity of the manganese dioxide is about 304 mAh/g. The amount of electric charge extractable in continuous discharge, however, ranges between 30 and 70 % depending on the current load. Great effort has been therefore devoted to improve the EMD discharge behavior modifying the synthetic procedure or by a post-synthesis treatment. Presented paper describes the effect of the solvothermal treatment of the EMD on its discharge behavior. Electrochemical characteristics gathered by galvanostatic discharge, galvanostatic cycling and linear scan voltammetry are related to results of the materials characterization using X-ray diffraction and vibration spectroscopy.

The electrolytic MnO_x (purity 92.2%, x=1.97, BET surface area 32 m^2/g) was obtained from CEGASA. The untreated sample was either hydrothermally treated in water at 200°C for 20 hours or vacuum dried at 180 °C fro 12 hours. All electrochemical tests were performed on electrodes composing of 89 % of MnO_x , 8% of graphite and 1% of PTFE suspension as a plastificator. Electrode mixture was pressed on Nickel mesh (Delker Corp.); the average mass of the prepared electrode was about 30 mg.

The post-synthesis treatment shows a pronounced effect on the continuous discharge of the EMD cathode. The vacuum dried material improves the attainable capacity of the cathode, on the other hand the hydrothermally treated material deteriorates the observed capacity. The difference in response of the cathode materials based on untreated and post-synthesis treated EMD decreases with decreasing current load. Besides of the change in the specific capacity the post-synthesis treatment causes also a decrease of the cathode potential during discharge process. Also linear scan voltammetry experiments show distinctive features attributable to post-synthesis treatment. The post synthesis treatment suppresses the EMD reduction related to the terminal surface oxygen atoms. On the other hand, the current signals corresponding to reduction of different phases are more pronounced for the electrodes based on post-synthesis treated EMD.

The difference in electrochemical behavior of different EMD samples is difficult to explain. The decrease of the electrochemical activity of hydrothermally treated material can be related to partial re-crystallization of the EMD to $Mn_2O_3 \cdot H_2O$. The voltammetric data also indicate that this process proceeds primarily at the account of the ramsdellite blocks. The vacuum dried material on the other hand shows no change of the crystalline structure. The total amount of surface hydroxyl groups is, however, decreased. Vibrational spectroscopy, in contrast to data shown in literature[1] is poorly sensitive to change in the structure (see Fig.3). The IR spectra show some response attributable to formation of $Mn_2O_3 \cdot H_2O$. Raman spectra, on the other hand do not show asuch a signal. This behavior may be explained by poor activity of the $Mn_2O_3 \cdot H_2O$ in Raman spectra.

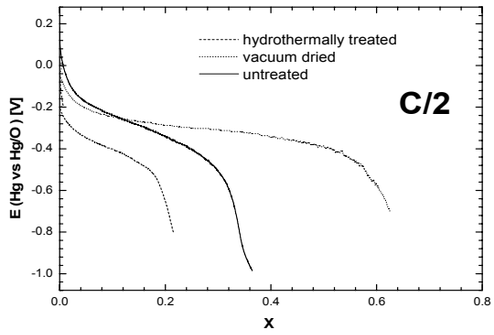

Figure 1 Potential vs. relative utilization curves for different EMD samples continuously discharged at C/2. Sample assignment is given in Figure inset.

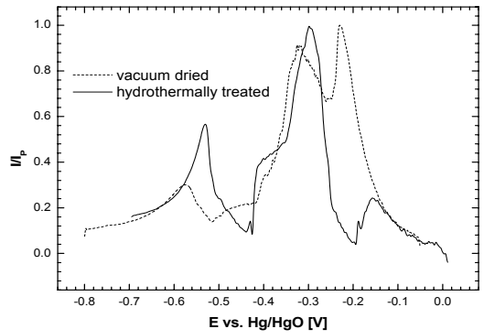

Figure 2 Linear scan voltammograms of different EMD samples. Polarization rate was 3μV/s. Sample assignment is given in Figure inset.

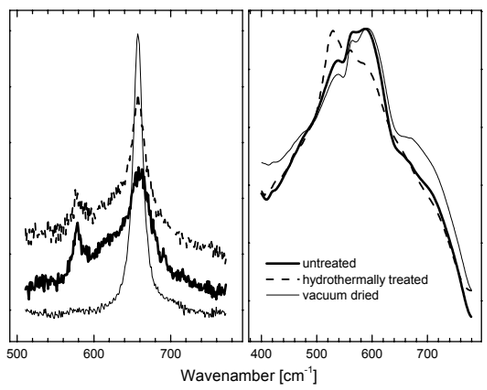

Figure 3 Raman (left) and infrared spectra (right) of different EMD samples. Sample assignment is given in Figure inset.

References

[1] C. Julien, M. Massot, S. Rangan, M. Lemal and D. Guyomard, *J. Raman. Spectr.*, **33**, (2002) 223.