Abstract #579, 223rd ECS Meeting, © 2013 The Electrochemical Society

Colloidal processing of MnO_2-carbon nanotube electrodes for electrochemical supercapacitors

M.S. Ata and I. Zhitomirsky

Department of Materials Science and Engineering
McMaster University

1280 Main Street West,
Hamilton, Ontario, Canada L8S 4L7

The electrochemical supercapacitors (ESs) are an emerging technology that promises to play an important role in meeting the demands of automotive and electronic industry. A notable improvement in ES performance has been achieved through recent advances in understanding charge storage mechanisms and the development of advanced nanostructured materials, such as nanostructured MnO_2 and composites.

The anodic electrophoretic deposition (EPD) method has been developed for the fabrication of MnO_2 and composite MnO_2-multiwalled carbon nanotubes (MWCNTs) films. The problem of low stability of MnO_2 suspensions was addressed by the development of new dispersing agents. The adsorption of the organic molecules on the MnO_2 nanoparticles involved the interaction of COOH groups and OH groups with Mn atoms on the particle surfaces and complexation. The results showed that adjacent OH groups, as well as adjacent OH and COOH groups bonded to the aromatic ring of the phenolic molecules enabled enhanced adsorption of the organic molecules. In this work, the results obtained for molecules with different numbers of OH groups, aromatic rings and different lengths of hydrocarbon chains were analysed and compared with corresponding experimental data for molecules with similar structure but without adjacent OH groups. It was demonstrated that the adsorption mechanisms of dispersing agent on MnO_2 nanoparticles involved the interaction of adjacent OH groups of organic molecules with Mn ions on the particle surfaces and complexation. Additionally, it was found that EPD of MnO_2 and MWCNTs can be achieved using by universal dispersants and charging additives.

New dispersion methods allowed the formation of composite electrodes by colloidal techniques, such as EPD or slurry impregnation of MnO_2 and MWCNTs into advanced current collectors, such as porous nickel foam and nickel plaque. MnO_2 and MWCNTs can form a porous network, which is beneficial for the electrolyte access to the active materials. The effect of the MWCNTs concentration, scan rate and electrodes type on the capacitive behaviour was discussed. It was found that the addition of MWCNTs can improve the capacitive performance of MnO_2 electrodes and reduced equivalent series resistance.

The deposition yield was studied by quartz crystal microbalance (QCM). The films were analyzed by Fourier transform infrared spectroscopy (FTIR), thermogravimetry analysis (TGA), differential thermal analysis (DTA), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The method allows co-deposition of different materials and control of deposit composition. The deposition yield measurements showed that the amount of deposited material can be controlled by variation of dispersant concentration in the solutions and deposition time. The deposition mechanism and kinetics of deposition are discussed.

The porosity of Ni plaque enabled for the fabrication of electrodes with higher materials loading. The comparison of the capacitive behaviour of the electrodes prepared using EPD methods showed that nickel plaque (185 Fg^{-1}) based electrodes have higher specific capacitance (SC) value than stainless steel (165 Fg^{-1}) electrode at a scan rate of 2 mVs^{-1}, for deposited mass 2.08 and 0.650 $mgcm^{-2}$. The significant differences were occurred at higher scan rates. The SC at 100 mVs^{-1} was found to be 98 and 30 Fg^{-1} for Ni plaque and stainless steel electrode, respectively. The electrochemical spectroscopy studies showed that the impedance of the Ni plaque based electrode was substantial lower than impedance of stainless steel based electrode.

The films prepared by EPD method are promising materials for application in ES.