Abstract #551, 223rd ECS Meeting, © 2013 The Electrochemical Society

Fabrication of MnO_2-CNT nanocomposites using universal dispersing agents

Yisong Su, Igor Zhitomirsky

Department of Materials Science and Engineering
McMaster University
1280 Main Street West,
Hamilton, Ontario, Canada L8S 4L7

The electrode of MnO_2 electrochemical supercapacitors (ES) is usually a composite film of MnO_2 nanoparticles and carbon nanotubes (CNT), where MnO_2 mainly contributes to the pseudocapacitance and CNT provides conductivity of the composite film. For the fabrication of ES, electrophoretic deposition (EPD) and slurry impregnation are vastly used in both industrial and academic fields because of their simple procedures, low cost, high purity etc. Both EPD and impregnation of current collectors from colloidal suspensions requires a mixed stable colloidal suspension of CNT and MnO_2 nanoparticles.

It is difficult to obtain stable suspension and EPD of CNT without introducing impurities (using surfactants) or structure damages (chemical functionalization), which will inevitably reduce CNT conductivity. The dispersion and EPD of pristine CNT is of great importance for the fabrication ES electrodes. It was found that small anionic or cationic organic molecules with aromatic rings can provide good dispersion and charging to CNT, and allowed EPD of CNT

For the dispersion and EPD of MnO_2, small organic molecules from catechol family and salicylic family are discovered. Both of them are good dispersant and charging agent for MnO_2 nanoparticles. And the mechanism related to this phenomenon is suggested the binding between catechol or salicylic groups and the surface of nanoparticles.

However, in a mixed suspension of both CNT and MnO_2, a dispersant working with CNT can cause the flocculation of MnO_2 and vice versa, which is because those extra dispersant molecules exist as free ions and hence promote the flocculation of colloidal particles in suspension. For this reason, co-deposition of both CNT and MnO_2 always results in poor dispersion of components and hence a low capacitance.

A universal dispersant is the one that can disperse CNT and MnO_2 simultaneously. Such dispersant can adsorb on the surface of both CNT and MnO_2 nanoparticles. So the dispersant can cause a binding force between them. As a result, the agglomeration of either CNT or MnO_2 can be prevented and a better mixed suspension can be obtained. Because only one dispersant is used, both CNT and MnO_2 nanoparticles have the same charge and hence can be deposited together on the same electrode through EPD, which results in a better mixture.

A universal dispersant is discovered, calconcarboxylic acid (CCA), with both aromatic rings to bind CNT and salicylic group to bind MnO_2 nanoparticles. As shown in Fig.1, CCA can disperse both MnO_2 nanoparticles and CNT to form stable suspension for several months. As comparison, suspensions of MnO_2 and CNT without CCA as dispersant precipitated as soon as the sonication stops and finished within several hours.

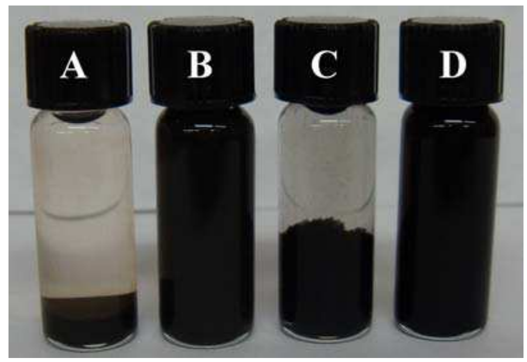

Fig.1 Suspensions of (A) MnO_2 (B) MnO_2 with CCA, (C) CNT (D) CNT with CCA.

By using EPD, a composite film with both MnO_2 and CNT can be obtained. CCA forms anions in ethanol, which allows anodic deposition of composite films. Using the universal dispersant, the morphology reveals a better mixture between CNT and MnO_2, which can utilize more pseudocapacitance of MnO_2 and hence results in a higher specific capacitance of the composite film (Fig.2). As a comparison, pure MnO_2 film has lower capacitive performance at all range of scanning rates. But with the increase of CNT concentration, the weight percentage of CNT increases and hence causes a reducing of specific capacitance.

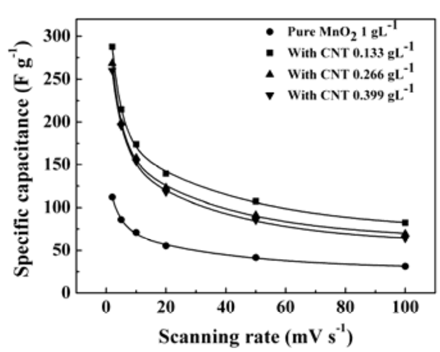

Fig.2 Specific capacitance versus scan rate of samples prepared from 1 gL^{-1} MnO_2 suspensions with different CNT concentrations, containing 0.2 gL^{-1} CCA.