Fabrication of novel hierarchical hollow manganese oxide nanospheres for high-voltage stability supercapacitors in aqueous electrolyte

Yu-Ting Weng Hsiao-An Pan, Rung-Chuan Lee and N. L. Wu

Department of Chemical Engineering,
National Taiwan University, Taipei 106, Taiwan, R.O.C.

Supercapacitors, also known as, electrochemical capacitors, have been known for several years and are considered as one of the potential energy storage systems in addition to batteries due to high power and reasonably good cycling stability. Supercapacitors that only involve physical adsorption of ions in this manner, without any chemical reactions, are called electrochemical double layer capacitors (EDLCs). In the case of pseudocapacitors, the charge storage is using redox-based Faradic reactions. Therefore, this pseudo-capacitance can be superimposed on any electric double-layer capacitance. In principle, pseudocapacitors can provide a higher energy density than EDLCs, but because the electrodes undergo physical changes during charge/discharge they have relatively poor cycling stability compared with EDLCs. The performance of a supercapacitor, in terms of energy and power densities, is governed mainly by the specific capacitance of the active electrode materials and the cell voltage. In additionally, high-voltage organic systems can store a high overall energy density; however, their power density is usually lower than that of aqueous electrolyte because the electric conductivity of organic electrolyte is relatively low.

Supercapacitors with nanostructured electrode materials have shown the potential to combine the high energy density and high power capabilities, but face important challenges related to durability, processability, cost and enrionmental effects for technology impact. Manganese oxide (MnO_2) chemistry has been widely attractive for energy storage applications comes from its low cost, availability in abundance, and environmental benignity. However, comparing with RuO_2, MnO_2 exhibits much lower capacitance with a typical value in the range of 150-200 F/g. In order to improve the performance of MnO_2, increasing the specific surface area is an effective way, and many efforts have been made on the synthesis of different nanostructured MnO_2, such as hollow spheres and hollow urchins, brinessite structure, nanosheets, nanowires/nanorods, nanotubes, nanoporous structure. Thus research on the preparation method to create nanostructure active materials is of great significance.

In this work, we have prepared hierarchical hollow MnO_2 by utilizing a templating-assisted hydrothermal process. Compared with general method, nevertheless, we do not dissolve the templating-SiO_2 totally. Consequently, it has to be stressed that residued-SiO_2 can be a framework to support MnO_2. The results revealed that the novel hollow nanostructure MnO_2 electrode had a specific capacitance as large as 890 F/g, and it unprecedentedly demonstrates good cycle stability, retaining 70% capacitance after 5000 cyclic stability, over a potential range of 0.8~-0.8 V vs. AgCl/Ag. X-ray absorption spectroscopy analysis further reveals the nature of two-phase reaction taking place over low-potential range. This outstanding hierarchical hollow MnO_2 nanosphere is promising electrode material for next generation high performance supercapacitor.

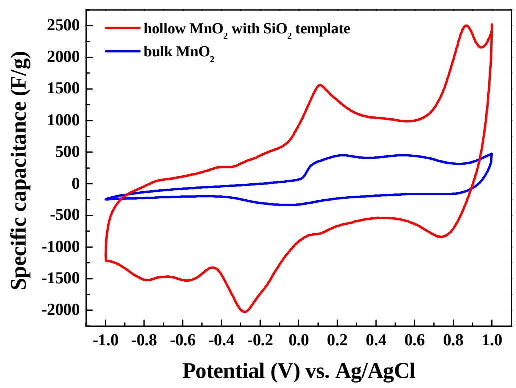

Figure 1. Cyclic voltammograms of MnO_2-containing electrodes at 2mV/sec by using 2M $Li_2SO_{4(aq)}$ as electrolyte.