

Electrochemical supercapacitor studies of nanostructured electrode based on ϵ/γ -MnO₂ synthesized by chemical reduction and electrochemical deposition

LE M.L.Phung, HA The An, TRAN Van Man

APC Lab, University of Science – Vietnam National University - Ho Chi Minh City (VNU-HCM), 227 Nguyen Van Cu street, district 5, Ho Chi Minh City, Vietnam

Corresponding author: lmlphung@hcmus.edu.vn

Nanostructured or nanometer-scale particle of several materials have been considerably attracted in recent years, as they possess properties more favorable in technological applications than microstructure or larger particle size. The large surface-to-volume ratio results in an increase in the chemical and electrochemical activity [1,2]. In the area of electrochemical reactions, which involve solid-state diffusion processes, nanoparticles are advantageous as they provide shorter diffusion path length than the corresponding materials of larger particles. Electrodes made of nanoparticles of MnO₂ are expected to offer high levels of material utilization for supercapacitor applications [3]. Over the years various nanostructured manganese oxides with different shapes: nanowires, nanotubes, nanoflowers, nanoflakes have been synthesized in attempt to increase the specific capacitance of materials nearby the theoretical value of 1100 F/g [4,5]. Besides, in order to greatly increase electrochemical performance of manganese oxides, a nanostructured composite electrode or hierarchical porous structure with high electronic conductivity must be considered. The porous architecture could be carbon nanofoams, template mesoporous carbon, nanographite and nanotube assemblies [5].

In this work, we have focused on structure design and synthesis of nanostructured MnO₂ by chemical reduction and electrochemical deposition. In chemical reduction, by using different template carbons (graphite, CNTs, Vulcan carbon, mesoporous carbon, Super P carbon), the microstructure and electrochemical performance of MnO₂/C composite electrodes changed. As shown on the SEM image (Fig.1), the surface morphology was completely changed with carbon structure. There are aggregates of particles without clear interparticle boundary. A rough estimation provides the particle size in 40 – 70 nm for MnO₂ composite electrode and in 200 – 300 nm for MnO₂ flower (Fig 1a). The XRD results indicate that ϵ -MnO₂ is a principal phase, however, the minor phase such as α -MnO₂ or γ -MnO₂ can be involved while using variety of carbon. In electrodeposition, thin films of MnO_x.nH₂O are deposited on stainless steel substrate by chronoamperometry method. The thickness and microstructure of MnO₂ films was controlled by MnSO₄ concentration, applied potential as well as time deposition.

For electrochemical measurements, the porous composite electrode material of MnO₂/C was shaped by using 60 wt% PTFE (polytetrafluorethylene) in ethyl alcohol as binder compound. Squares (1cm²) of the composite active material paste were cut and placed between two stainless steel grids to be pressed under 10 tons for two minutes. The specific capacitances (C_{sp}) of the prepared electrodes were determined by cyclic voltammetry measured in aqueous 2 M Na₂SO₄ and in 0.1M

TEABF₄/acetonitrile at different potential scan rates: 1, 5, 10, 25 and 50 mV/s. The electrochemical properties of thin film MnO₂ was compared to those of chemical reduced MnO₂ (CMD). Thin film MnO₂ exhibited C_{sp} significantly higher than CMD based electrode due to its high porosity and homogenous surface and thickness. In addition, the charge transfer resistance is lower than CMD. In contrast, compared to pure MnO₂ capacitance, those for composite electrodes (with 30 wt% carbon) is 25 % higher. Using CNTs combined with Vulcan carbon enhanced significantly the C_{sp} of MnO₂/C electrode, up to 30% higher at 5 wt% CNTs added than initial value of only Vulcan carbon in composite electrode. All samples exhibited good cycling behavior, less than 10% capacitance loss after 300 cycles. The charge – discharge test was performed by using symmetric configuration in Swagelok cell. The results will be further discussed.

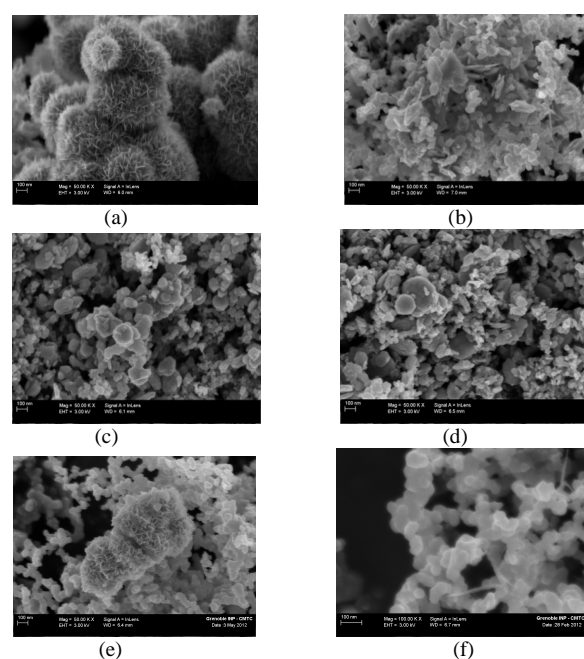


Figure 1: SEM images of manganese oxide-based electrodes prepared by chemical reduction (a) MnO₂ (CMD); (b) MnO₂/graphite; (c) MnO₂/mesoporous carbon; (d) MnO₂/Vulcan carbon; (e) MnO₂/super P carbon; (f) MnO₂/Vulcan – 5% wt CNTs

Acknowledgements

This work was supported by Vietnam National University – Ho Chi Minh City through the Science and Technology Fund granted for the B2011-18-01 TD.

References

- [1]. Antonino. S. Arico et al., Nature Materials. 4 (2005) 366.
- [2]. B. L. Cushing et al, Chem. Rev. 104 (2004) 3893.
- [3]. S. Devaraj et al., J. Electrochem. Soc. 154 (2007) A80.
- [4]. P. Simon et al., Nature Materials 7 (2008) 845.
- [5]. W. Wei et al., Chem. Soc. Rev. 40 (2011) 1697.