Characterization of Spray Pyrolyzed Manganese Oxide Powders Deposited by Electrophoretic Deposition Technique

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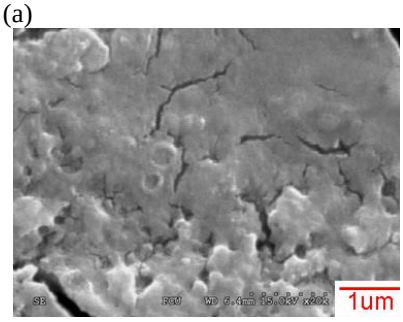
Supercapacitors has been stimulated by their potential application as electric storage devices that provide high power transiently. Manganese oxides, where the manganese can exhibit in various valence states, are promising supercapacitor materials due to the low cost of raw materials and the fact that manganese is considered environmentally more friendly than other nobel metal oxides.

In the present work, nanocrystalline manganese oxide powders were prepared by spray pyrolysis from manganese acetate solution at 400 °C. The powders were coated onto graphite substrates by electrophorectic deposition. The as-deposited films were examined by scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), and cycling voltammetry (CV), etc. Experimental results showed that manganese oxide powders prepared at 400 °C were hollow spherical particles with fractured shells and possessed the highest surface area, Fig. 1(a). CV examination showed that the as-deposited coatings exhibited a high specific capacitance of ~270 F/g. After CV tests (Fig. 1(b), the porous structure have destroyed and degraded the supercapacitive performance of the manganese oxide films.

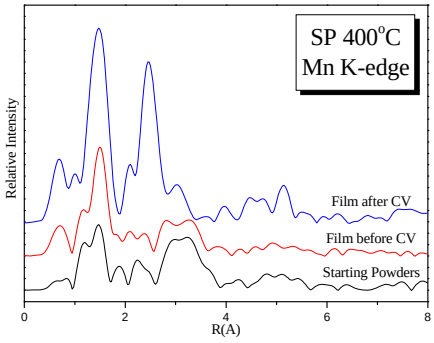
(a)



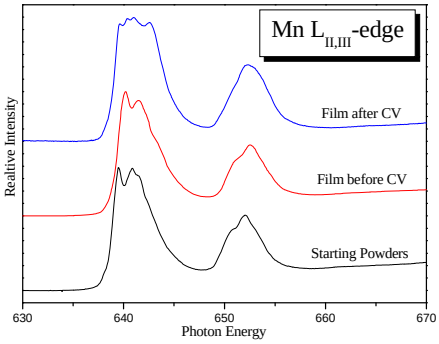
(b)

Figure 1. SEM photos of manganese oxide films (a) before and (b) after CV tests.

Synchrotron X-ray absorption spectroscopy studies was used to evaluate the electrochemical behavior of manganese oxide films before and after CV tests. Figure 2(a) shows the radial distribution functions (RDFs) of manganese at various stages (starting powder, as-prepared films and films after CV tests). It can be noted that the starting powder and as-prepared films exhibited similar RDFs, but significant differences can be observed after CV tests. According to X-ray diffraction results, the previous two exhibited Mn_3O_4 phase, while Mn_3O_4 to MnO_2 transition may occur during CV tests. Figure 2(b) reveals the manganese electronic structures of the corresponding samples examined in Fig. 2(a). An obvious intensity increase for the peak at ~643 eV (corresponding to Mn^{4+} ion) can be observed after CV tests. This confirmed the formation of MnO_2 phase, at least on the surface, during CV tests. Synchrotron XAS results showed that the manganese with a valence of +2.67 (Mn_3O_4) was transited into tetravalent manganese (MnO_2) after cyclic voltammetry.



(a)



(b)

Figure 2. (a) Radial distribution functions and (b) XANES spectra of manganese oxide films.

*****C. Y. Chen, Y. R. Lyu, C. Y. Su, H. M. Lin, and C. K. Lin, Surf. Coat. Technol. **202**, 1277-1281 (2007).