Electrochemical and Textural Characterization of Manganese Oxide-Based Electrodes for Electrochemical Supercapacitors

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Introduction

Due to the cost consideration, MnO_2 thin films prepared by sol-gel or electrochemical deposition methods were found to exhibit excellent capacitive properties in neutral media,[1-5] which generally have specific capacitance of 50~250 F/g although a very thin MnO_2 film prepared by a sol-gel-derived method was found to show a very high specific capacitance of ca. 700 F/g (based on the loading of MnO_2).[6] In our previous work,[1, 7] thin manganese oxide deposits (<1 μm) prepared by electrochemical deposition in approximately neutral media showed the ideally capacitive characteristics for supercapacitors while its capacity is not very high. In addition, the conductivity of thick MnO_2 was found to be too low to be a suitable electrode material,[3, 8] which resulted in a relatively poor performance of Mn oxide in the thick nature. Thus, how to optimize the capacitive performance of MnO_2-based electrodes is an interesting and important work for the development of super- capacitors.

Results and Discussion

Various deposits plated by the potentiostatic mode at 1.0 V from a 0.1 M $Mn(CH_3COO)_2{\cdot}4H_2O$ solution with the deposition time of 5, 10, 15, 20, 30 and 40 min were employed to investigate the effect of oxide thickness on the electrochemical characteristics of a-$MnO_x{\cdot}nH_2O$. In addition, these oxide deposits were respectively denoted as a-$MnO_x{\cdot}nH_2O$-5, a-$MnO_x{\cdot}nH_2O$-10, a-$MnO_x{\cdot}nH_2O$-15, a-$MnO_x{\cdot}nH_2O$-20, a-$MnO_x{\cdot}nH_2O$-30 and a-$MnO_x{\cdot}nH_2O$- 40. Typical CV results measured in 0.1 M Na_2SO_4 at 25 mV s^{-1} are shown in Fig. 5. Note that the electrochemical responses of a-$MnO_x{\cdot}nH_2O$-5, a-$MnO_x{\cdot}nH_2O$-10 and a-$MnO_x{\cdot}nH_2O$-15 (see curves 1-3) show the rectangular- like and symmetric behavior. In addition, voltammetric currents on these curves increasing with prolonging the deposition time, revealing the fact that electric energy stored within these deposits is mainly contributed by the redox transitions of a-$MnO_x{\cdot}nH_2O$ (i.e., pseudo- capacitance). All these results reveal the ideality of capacitive performance for a-$MnO_x{\cdot}nH_2O$ deposited by electrochemical modes. However, the above phenomena are not found for curves 4-6, demonstrating the influence of oxide thickness. The voltammetric responses of a-$MnO_x{\cdot}nH_2O$-20 (see curve 4) are rugby-like rather than rectangular-like, indicating a decay in the electrochemical reversibility. Note that the voltammetric charges surrounded by curves 5 and 6 corresponding to a-$MnO_x{\cdot}nH_2O$-30 and a-$MnO_x{\cdot}nH_2O$-40 are unexpectedly smaller than that corresponding to a-$MnO_x{\cdot}nH_2O$-20. In addition, a heavier loading of a-$MnO_x{\cdot}nH_2O$ is, the smaller voltammetric charge the deposit has. Based on this result, there should exist a limitation on the capacity of a-$MnO_x{\cdot}nH_2O$ deposits for the application of supercapacitors. The decay in the electrochemical reversibility of a-$MnO_x{\cdot}nH_2O$ with prolonging the deposition time probably results from the increase in ESR (equivalent series resistance) for a heavier deposit because of the poor conductivity of amorphous MnO_2[3, 8] and/or the significance of proton diffusion barrier on this deposit.

References

1. C.-C. Hu, T.-W. Tsou, *Electrochem.Comm.*, **4**, 105 (2002); *Electrochim. Acta*, **47**, 3523 (2002); *J. Power Sources*, **115**, 179 (2003).
2. J.-K. Chang, W.-T. Tsai, *J. Electrochem. Soc.*, **150**, A1333 (2003).
3. H. Y. Lee, J. B. Goodenough, *J. Solid State Chem.*, **144**, 220 (1999).
4. J. Jiang, A. Kucernak, *Electrochim. Acta*, **47**, 2381 (2002).
5. Y. U. Jeong, A. Manthiram, *J. Electrochem. Soc.*, **149**, A1419 (2002).
6. S.-C. Pang, M. A. Anderson, T. W. Chapman, *J. Electrochem. Soc.*, **147**, 444 (2000).
7. C.-C. Hu, C.-C. Wang, *J. Electrochem. Soc.*, **150**, A1079 (2003).
8. H. Kim, B. N. Popov, *J. Electrochem. Soc.*, **150**, D56 (2003).

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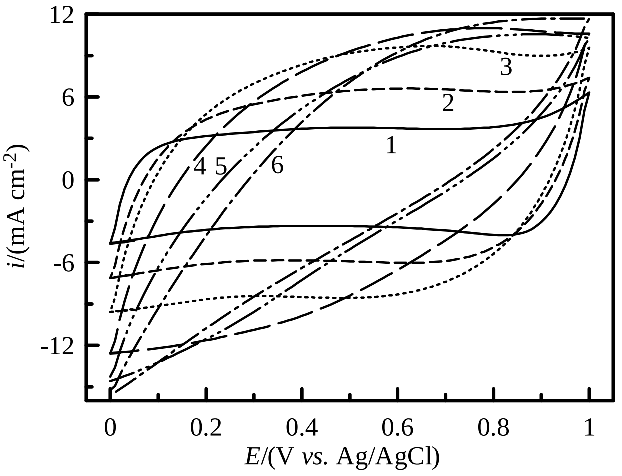

Fig. 1 CV curves of a-$MnO_x{\cdot}nH_2O$ measured in 0.1 M Na_2SO_4 at 25 mV s^{-1}. All deposits were prepared from $Mn(CH_3COO)_2{\cdot}4H_2O$ by a potentiostatic mode at 1.0 V for (1) 5; (2)10; (3) 15; (4) 20; (5) 30; and (6) 40 min.