Development of Low Cost Composites for Supercapacitors

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Introduction

For the supercapacitor materials, RuO_2 has perfect characterizations except for its high cost.1 In addition of expensive noble materials itself, due to strong acid electrolyte used a current corrector also should be another expensive noble materials. To satisfy low cost materials for supercapacitors, alternative low cost materials were suggested such as Mn,[2] Ni,[3] Co, and Ti-V-W oxides[4]. However, these materials have a small capacitance or limited potential window due to instability.

In this study, Mn based alloy materials were synthesized in order to increase the specific capacitance and energy density at high power discharge by increasing the stability of MnO_2.

Experimental

Mn based alloy oxides of $X_{1-y}Mn_yO_2{\cdot}nH_2O$ (X = Pb, W, Cr, Co) were prepared by reducing the salts of each material.

The electrodes were fabricated by mixing 75w% of active material, 20wt% of carbon black (Black pearls 2000, Cabot Corp) and 5 wt% PTFE. Pellet type electrodes (ϕ = 0.8 mm, 9 mg) were cold pressed between two titanium grids.

Electrochemical measurements were carried out using an EG&G PAR Model 273A. SCE and Pt plate were used as a reference electrodes and a counter electrode, respectively. Cyclic voltammograms were obtained in a 1M Na_2SO_4 solution. The capacitance, C, of $Ru_{1-x}Mn_xO_2{\cdot}nH_2O$ electrode was calculated from CV curves by $C = i/s$ where i and s denotes the current response and the scan rate, respectively. SEM, EDS, BET and XRD were also used to characterize the $X_{1-x}Mn_xO_2{\cdot}nH_2O$ electrode.

Results and Discussion

The potential window of operating the electrode of MnO_2 prepared by the reduction between $KMnO_4$ and $(CH_3CO_2)_2Mn$ was tested in 1M Na_2SO_4. With increasing potential window over 0.7V and below 0V vs. SCE high peak current was observed. This peak mainly comes from the hydrogen and oxygen evolution reactions. When cycle life test was done where peak current was appeared, its capacitance decreased continuously with cycling. Besides the cycle life problem, the gas evolved during reaction can increased the pressure inside of cell and cause the safety problem.

To increase the stable potential window by avoiding the peak current, several elements were introduced to make alloy. One of the tries, Pb was tested because Pb is known to have high overpotential of hydrogen and oxygen overpotential. By alloying with Pb its stable potential window increased by 200mV and showed good cycle life in this potential area as shown in Fig. 1. Its specific capacitance also increased from 158 F/g to 186 F/g according to the constant current discharge of 120mA/g. Fig. 2 shows the energy density of carbon, MnO_2 and Mn/PbO_2 at the constant power discharge of 700 W/Kg. After alloying with Pb, the energy density of Mn/PbO_2 increased by 80% compared to MnO_2 because energy density depends on the square of potential difference. The annealing temperature effect and optimum ratio of Mn and Pb will be discussed. On the top of that, the capacitive behavior of the other alloy materials will be tested.

References

1. J. P. Zheng, P. J. Cygan and T.R.Jow, *J. Electrochem. Soc*., **142**, 2699 (1995).
2. H. Y. Lee and J. B. Goodenough , *J. of Solid State Chem*., **148**, 81-84 (1999).
3. V. Srinivasan and J. W . Weidner., *J. Electrochem. Soc*., 144, L210 (1997).
4. Y. Takasu, S. Mizutani, M. Kumagai, S. Sawaguchi and Y. Murakami, *Electrochem. and Solid State letters*, **2**(1) 1-2 (1999)

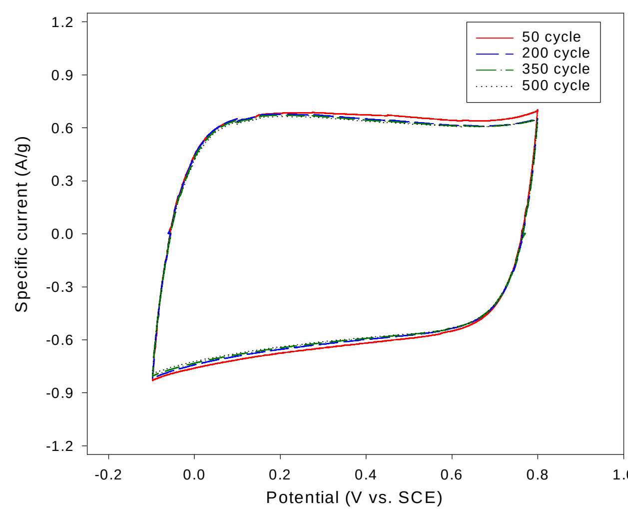

Fig. 1 Cycle life test of Mn/PbO_2 using cyclic voltammogram (1M Na_2SO_4, 5mV/s, -0.1 ~ 0.8V)

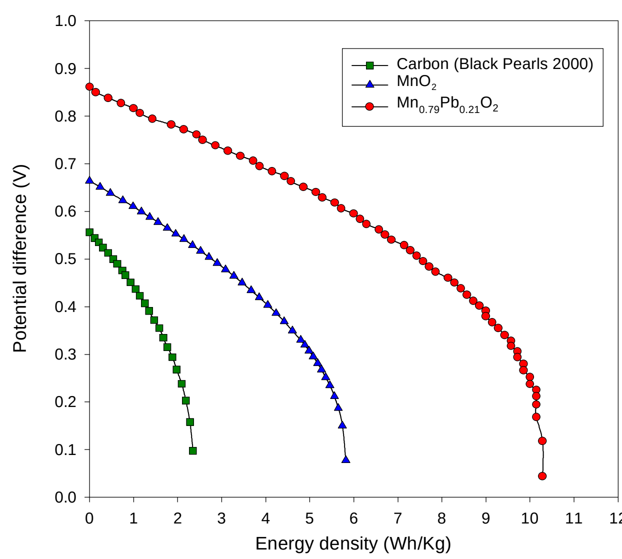

Fig. 2 Discharged energy density curves of the single electrodes at the constant power density of 700W/Kg