

A Mathematical Model of Composite Electrode for Supercapacitors

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Introduction

Various mathematical models have been developed for analyzing the behavior of double layer capacitors. Posey and Morozumi¹ reported macroscopic equations to explain the behavior of double layer capacitors under potentiostatic and galvanostatic charging in porous electrodes. Johnson and Newman² developed a model to describe double layer charging in an electrochemical cell and to predict the specific energy and power densities of electrochemical capacitors. Pillay and Newman³ modeled the influence of side reactions on the performance of electrochemical capacitors. Srinivasan and Weidner⁴ presented an analytical solution of the double layer capacitor under two types of operating conditions: (i) constant current and (ii) electrochemical impedance spectroscopy.

In the case of pseudocapacitance, few models have been developed. This model should consider the faradaic reaction occurring on the transition metal oxide. Lin et al.⁵ developed the capacitor model considering both double layer capacitance and pseudocapacitance. This model explained the effect of the particle size of oxide and of the cell current density on the charge/discharge behavior. However, this model assumed that the concentration of electrolyte in the electrode does not change and faradaic processes take place only on the external surface of the particles. This simplification can be removed by considering the concentrated solution theory and the diffusion of working ions in the particles presented by Doyle et al.⁶

Model description

Figure 1 shows a schematic of a typical supercapacitor cell. Two identical composite porous electrodes consisting of active carbon and RuO₂ are separated by an ionically conductive glass fiber. The total current is the sum of the contribution of the pseudocapacitance occurring on the transition metal oxide and the double layer (DL) capacitance of carbon together and can be expressed as follows.

$$\frac{\partial i_2}{\partial x} = S_d C_d \frac{\partial(\Phi_1 - \Phi_2)}{\partial t} + S_f j_f$$

where i_2 is the superficial current density in the electrolyte phase. S_d is the specific surface area for double layer capacitance per unit volume and S_f is the specific surface area for pseudocapacitance per unit volume. C_d is the DL capacitance per area. Φ_1 and Φ_2 are the potential of solid matrix and electrolyte phase respectively. j_f is the faradaic current by pseudocapacitance expressed by Butler-Volmer kinetics. In this model, a porous electrode theory was used in order to account for porosity and particle size effects on supercapacitor performance.⁷ In order to explain the variation of electrolyte concentration in the electrode, the concentrated solution theory⁷ was applied and the current distribution in the electrolyte phase is expressed by

$$i^2 = -\kappa^p \frac{\partial \Phi^2}{\partial x} - \frac{\kappa^p RT}{F} \left(1 + \frac{\partial(\ln f_{\pm})}{\partial(\ln C)} \right) \left(\frac{s^+}{t^+} + \frac{0}{t^+} \right) \frac{\partial(\ln C)}{\partial x}$$

where κ_p is ionic conductivity and f_{\pm} is electrolyte activity coefficient.

The bulk reaction occurring within the transition metal oxide was considered by the process of diffusion of oxidation state involving proton and electron hopping.⁸ The equations describing the system were solved numerically using DASPK solver simultaneously.

Results and Discussion

The preliminary simulation data showed the effects of the divers factors related to packing condition in the electrode such as the composition ratio between carbon and oxide, the particle size of oxide and carbon and porosity of the electrode. According to our previous experimental data, it was found to have an enormous effect on the performance of supercapacitors.⁹ High amount of carbon contained in the electrode increases the porosity of electrode. It is helpful for reducing the depletion of electrolyte at high current discharge mode. However, the total specific capacitance of electrode decreases as the carbon ratio increases beyond a certain level since the specific capacitance is lower than RuO₂. And it also showed that smaller particle size of RuO₂ is favorable to get higher rate capability because of limitation of proton diffusion in the oxide particle.

This model can be used to design the optimum condition of supercapacitors in order to improve the energy density and power density at the high rate discharge rate.

References

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Current Collector

