THE LIMITATIONS OF ENERGY DENSITY FOR BATTERY/DOUBLE LAYER CAPACITOR HYBRID CELL

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In the electrochemical (EC) capacitor research, much effort has been focused on the development of high energy density devices. However, the low operating potential window in aqueous electrolyte system, or low specific capacitance and low salt concentration in non-aqueous system limit the maximum energy density (e.g. less than *27 Wh/kg* based on active materials only) of EC capacitor [1]. Recently, battery/EC capacitor cells were introduced in order to improve the energy density and at the time to maintain extended cycle life and fast charge capability [2-3]. In this paper, a model for estimating the maximum energy density and the voltage swing of hybrid cells is established. The model provides a useful tool for optimizing the energy density and mass ratio between two electrodes during the design of hybrid cell.

Figure 1 shows schematic potential changes of positive (EC capacitor) and negative (battery) electrodes in a hybrid cell. During the charge process, a non-faradaic reaction in activated carbon positive electrode causes a linear increase in potential; while a faradaic intercalation in negative electrode occurs at a constant potential. The maximum energy storage in the cell is limited by either positive or negative electrodes depended on the mass (m_C) and specific capacitance (c_C) of positive electrode, mass (m_B) and specific capacity (c_B) of negative electrode, and the maximum operating potential range (V_M). It can be provided that when $m_B c_B < m_C c_C V_M$, the energy density of the cell based on the weight of electrodes and electrolyte can be expressed as:

$$\varepsilon = (V_M - \frac{c_B}{2c_C}\gamma)\frac{\gamma c_B}{1+\gamma(1+\alpha)} \qquad (1)$$

where $\gamma = m_B/m_C$ is the mass ratio, $\alpha = \rho c_B/c_o F$ is a dimensionless parameter, ρ is the mass density of the electrolyte, c_o is the salt concentration of the electrolyte, and F is the Faraday's constant. The voltage swing (V_C) of the cell is also dependent on the mass ratio and can be expressed as:

$$V_c = \gamma\frac{c_B}{c_C} \qquad (2)$$

It can also be proved that the maximum energy density can be obtained at a mass ratio of

$$\gamma_{max} = \frac{1}{1+\alpha}\left[\sqrt{1+\frac{2c_C(1+\alpha)V_M}{c_B}} - 1\right] \qquad (3)$$

When $m_B c_B > m_C c_C V_M$, the total energy storage will be limited by the positive electrode. The voltage swing of the cell is V_M and the energy density of the cell will be:

$$\varepsilon = \frac{1}{2}c_C V_M^2 \frac{1}{(1+\beta)+\gamma} \qquad (4)$$

where $\beta = \rho c_C V_M/c_o F$. Figures 2 and 3 show the energy density and voltage swing as a function of the mass ratio for a cell made with activated carbon positive electrode (c_C=*100F/g*), $Li_4Ti_5O_{12}$ negative electrode (c_B=*160mAh/g*) [2], 1 M $LiPF_6$ in EC/DMC electrolyte, and the maximum operation potential range of V_M=*3V*. From Figure 2, it can be seen that the energy density increases with increasing mass ratio and reaches a maximum value of *30 Wh/kg* at the mass ratio of 0.255. At the maximum energy density, the voltage swing of the cell is 1.47 V. From Figure 3, it can be seen that voltage swing increases with increasing the mass ratio, and when γ>0.521, the total energy storage in the cell is limited by the positive electrode and ripple voltage is a constant of *3V*.

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[2] G. G. Amatucci, F. Badway, A. D. Pasquier, and T. Zheng, *J. Electrochem. Soc*. **148**, A930 (2001).
[3] A. Laforgue, P. Simon, J. F. Fauvarque, J. F. Sarrau, and P. Lailler, *J. Electrochem. Soc*. **148**, A1130 (2001).

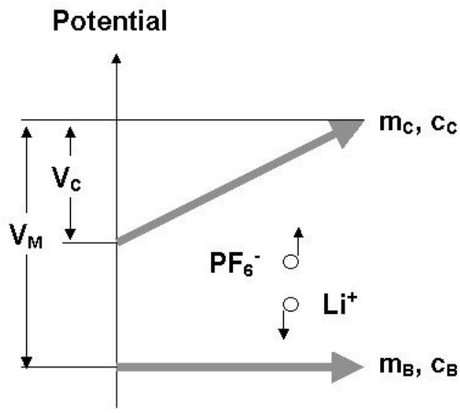

Figure 1 Schematic potential changes of double layer and intercalation electrodes during the charge process.

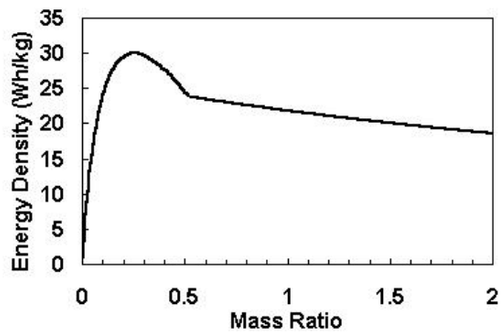

Figure 2 The energy density as a function of mass ratio for an activated carbon/$Li_4Ti_5O_{12}$ cell.

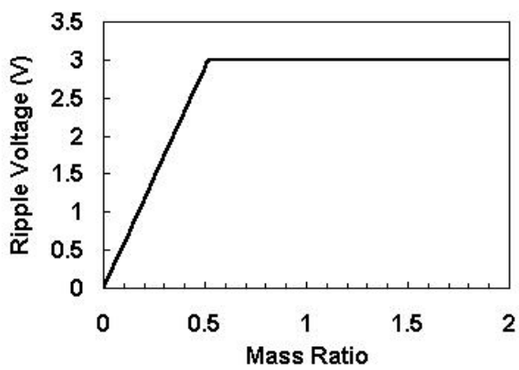

Figure 3 The voltage swing as a function of mass ratio.