A Mathematical Model for a Lithium-ion Battery/Electrochemical capacitor Hybrid System

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Introduction:

The high power density of electrochemical double layer capacitors makes them the most suitable power sources for high powered applications such as electric vehicles, power distribution systems, uninterrupted power supplies, hybrid vehicles and other electronic devices.[1,2] Despite the high power densities of electrochemical double layer capacitor, the energy densities of such capacitors are very less in comparison with high energy battery systems like Li-ion. Although the phenomenon of energy-power relationships between advanced battery systems and double layer electrochemical capacitors are contrasting to each other their combination may be utilized as power sources in a complimentary way. The objective of this presentation is to develop a mathematical model to simulate the performance of a battery-electrochemical capacitor hybrid system and to analyze the improvement in performance of the hybrid system compared to that of a battery alone under high current pulse loads.

Model Development:

The model system considered in this work has a lithium-ion battery in parallel with an electrochemical double layer capacitor. The battery consists of a porous $LiCoO_2$ cathode and a LiC_6 anode with small amounts of binder and conductive material. The electrodes are sandwiched using a polypropylene separator which is ionically conducting but electronically insulating and filled with 1M $LiPF_6$ in an EC/DMC mixture. For the case of the electrochemical capacitor, it has three regions with two identical porous carbon electrodes which act as anode and cathode, separated by an ionically conductive separator. The current distribution in the current collectors is ignored in both the capacitor and the battery and hence the ends of the anode and cathode act as boundaries. The assumptions made in the battery part of the hybrid model are summarized as: *(i)* one dimensional; *(ii)* D, t^+ are constant with respect to concentration; *(iii)* temperature effects with the cell are neglected; *(iv)* volume changes associated within the cell are neglected and hence constant porosities are considered. For the case of the electrochemical capacitor the assumptions involved are *(i)* one dimensional, constant transport properties in the solution phase; *(ii)* pseudo-capacitance is neglected and the energy storage mechanism is completely due to the charging of the double layer; *(iii)* concentration gradients in the solution phase is ignored; *(iv)* temperature changes within the cell are ignored. The pulse discharge current is shared between the battery and the capacitor based on the resistances across either component.

Results and Discussion:

The major advantage of the hybrid system over that of the battery system is its increased runtime over the battery under pulse loads. The run time extension of the hybrid system, which is defined as the ratio of the increase in the run time of the hybrid system over that of the battery system to the run time of the hybrid is plotted against the duty ratios for varying frequencies in **Figure 1.** Simulated results show that the run time extension increases with the increase in pulse frequency over the entire range of duty ratios. However for a given frequency (υ = 0.01 Hz), the run time extension had a peak at around a duty ratio, ψ = 0.2 and with the increase in frequency the peak shifts towards higher duty ratios. This is in close agreement with the experimental results reported by Sikha and Popov[3]. At the limit of $\psi \rightarrow 0$ the run time, $\tau \rightarrow \infty$ and hence the run time extension is theoretically zero. When $\psi \rightarrow 1$, the run time of the battery and the hybrid system is almost the same, but for a small increase in run time of the hybrid system due to the discharge of the capacitor which occurs during the initial part of the discharge. The current shared between the electrochemical capacitor and the battery has been predicted for various operating conditions such as frequency, duty ratio and peak pulse current. An extensive analysis of the effect of the number of capacitors added to the battery has also been performed based on the parameter, capacitor configuration index, Λ.

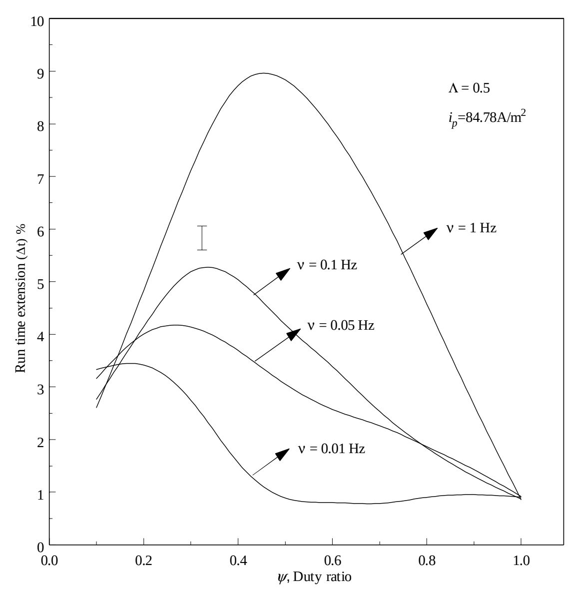

Figure 1. Simulated values of the percentage increase in the run time of the hybrid system over that of the battery system for different values of duty ratio. The effect of frequency on the run time extension of the hybrid system is also shown.

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List of Symbols:

υ - Frequency of pulse current, s^{-1}
Λ - Capacitor Configuration Index (no of capacitors in parallel to the number of capacitors in series in the hybrid system)
ψ - Duty ratio of the pulse current.

References:

1. B.E.Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications.* New York :Kluwer-Plenum, (1999).
2. R.Kotz and M.Carlen, *Electrochim. Acta*, **45**, 2483 (2002).
3. G. Sikha and B.N.Popov, *J.Power Sources.(in press)*