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Charging and discharging electrochemical supercapacitors in the presence of both parallel leakage process and electrochemical decomposition of solvent

Shuai Ban[a], Jiujun Zhang[a,*], Lei Zhang[a], Ken Tsay[a], Datong Song[a], Xinfu Zou[b]

[a] *National Research Council of Canada, Vancouver, BC, Canada V6T 1W5*
[b] *Department of Applied Mathematics, University of Western Ontario, London, ON, Canada N6A 5B7*

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ABSTRACT

Simple models for electrochemical supercapacitors are developed to describe the charge–discharge behaviors in the presence of both voltage-independent parallel leakage process and electrochemical decomposition of solvent. The models are validated by experimental data collected using a symmetric two-electrode test cell with carbon powder as the electrode layer material and stainless steel as the current collector.

1. Introduction

Electrochemical supercapacitors (ESs) are considered important energy efficiency devices for rapid energy storage and delivery. Among the advantages of ESs are high power density, long lifecycle, high efficiency, wide range of operating temperatures, environmental friendliness, and safety. ESs also serves as a bridging function for the power/energy gap of traditional dielectric capacitors. These characteristics have made ESs very competitive for applications in electric hybrid vehicles, digital communication devices such as mobile phones, digital cameras, electrical tools, pulse laser technique, uninterruptible power supplies, and storage of the energy generated by solar cells [1–3]. Unfortunately, there are still some challenges, such as low energy density, high cost, and high self-discharge rate, which have limited wider applications of ESs [3,4].

In order to increase energy density, according to the energy density expression $E = 1/2CV^2$, where E is the ES's energy density, C is the specific capacitance, and V is the cell voltage, respectively, two major approaches have been taken. One is to increase the specific capacitance (C) of the electrode material [3–6], and the other is to increase the cell voltage (V) using solvents such as non-aqueous and ionic liquid solutions which have wider electrode potential windows [4,7–9]. From the energy density equation mentioned above, it is obvious that increasing cell voltage to enhance energy density is more effective than increasing the specific capacitance because the voltage is squared in the formula. However, if the cell voltage is too high, the electrochemical decomposition of solvent may occur due to the limited electrode material stability and/or solvent's thermodynamic decomposition windows. This solvent electrochemical decomposition could produce gaseous products, leading to the pressure build-up inside the cell, causing safety concerns, and self-discharge [10–17]. Another challenge of supercapacitors is the parallel leakages, causing a fast self-discharge, reducing the shelf-life. The main contributors to the parallel leakages of the supercapacitors can be summarized into four processes [7]: (1) Faradaic reaction of electrolyte impurities; (2) parasitic redox reactions involving impurities (oxygen groups and metals); (3) non-uniformity of charge acceptance along the surface of electrode material pores; and (4) possible short-circuit of the anode and cathode from improperly sealed bipolar electrodes. Due to these parallel leakages, the shelf-life could be significantly reduced when compared to those of electrochemical batteries [7].

To better understand the effects of parallel leakage process and/or electrochemical decomposition of solvent on supercapacitors' performance, some experimental and theoretical studies have been carried out to investigate the charge and discharge behaviors [18–23]. Since the parallel leakage process and the solvent decomposition are mainly related to the electrochemical

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* Corresponding author at: 4250 Wesbrook Mall, Vancouver, B.C. V6T 1W5, Canada. Tel.: +1 604 221 3087; fax: +1 604 221 3001.
E-mail address: jiujun.zhang@nrc.gc.ca (J. Zhang).

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Nomenclature

Symbol	*Meaning*
α_n	electron transfer coefficient in the rate determining step of negative electrode reaction
α_p	electron transfer coefficient in the rate determining step of positive electrode reaction
b_n	Tafel slope of the negative electrode reaction
b_p	Tafel slope of the positive electrode reaction
C	capacitance ($\mathrm{F\,cm^{-2}}$)
C_{dl}	double-layer capacitance ($\mathrm{F\,cm^{-2}}$)
C_m	specific capacitance ($\mathrm{F\,g^{-1}}$)
C_s	mole concentration of the solvent ($\mathrm{mol\,cm^{-3}}$)
ΔV^o	$= V_p^o - V_n^o - b_p \ln\left(i_p^o\right) - b_n \ln(i_n^o)$
e^-	electron
E	energy density ($\mathrm{Wh\,cm^{-2}}$)
$(E_m)_{\max}$	maximum energy density of the supercapacitor ($\mathrm{Wh\,kg^{-1}}$)
F	Faraday's constant (96,487 $\mathrm{C\,mol^{-1}}$)
i_F	current density induced by the solvent electrochemical decomposition ($\mathrm{A\,cm^{-2}}$)
i_n	current density of the negative electrode reaction ($\mathrm{A\,cm^{-2}}$)
i_p	current density of the positive electrode reaction ($\mathrm{A\,cm^{-2}}$)
i_{sc}	charging or discharging current density of the supercapacitor ($\mathrm{A\,cm^{-2}}$)
I_{cell}	constant current density for charging or discharging the supercapacitor ($\mathrm{A\,cm^{-2}}$)
k_n	reaction constant of the negative electrode reaction ($\mathrm{cm\,s^{-1}}$)
k_p	reaction constant of the positive electrode reaction ($\mathrm{cm\,s^{-1}}$)
m	mass of the electrode material (g)
$n_{\alpha n}$	electron transfer number in the rate determining step of negative electrode reaction
$n_{\alpha p}$	electron transfer number in the rate determining step of positive electrode reaction
n_n	overall electron transfer number in the negative electrode reaction
n_p	overall electron transfer number in the positive electrode reaction
p_n	product of the negative electrode reaction
p_p	product of the positive electrode reaction
$(P_m)_{\max}$	maximum power density of the supercapacitor ($\mathrm{W\,kg^{-1}}$)
R	universal gas constant (8.314 $\mathrm{J\,K^{-1}\,mol^{-1}}$)
R_{esr}	equivalent series resistance of the supercapacitor ($\Omega\,\mathrm{cm^2}$)
R_{lk}	equivalent leakage resistance ($\Omega\,\mathrm{cm^2}$)
S	reactant of the solvent
t	time (s)
t_{fd}	time needed for a supercapacitor being fully discharged (s)
T	temperature (K)
T_s	time needed when the supercapacitor voltage goes down to 95% of its maximum voltage (*s*)
V	voltage (V)
V_{cell}	voltage of the supercapacitor cell (V)
$V_{cell}^{\max}$	maximum voltage of the supercapacitor cell (V)
V_F	voltage induced by the solvent electrochemical decomposition (V)
V_n	negative electrode potential of the solvent electrochemical decomposition (V)
V_n^o	standard electrode potentials for negative electrode reaction (V)
V_p	positive electrode potential of the solvent electrochemical decomposition (V)
V_p^o	standard electrode potentials for positive electrode reaction (V)
V_{sc}	supercapacitor voltage (V)
$V_{sc}^{\max}$	designed charging voltage of the supercapacitor (V)
V_{sc}^o	maximum supercapacitor voltage (V)

processes occurring inside the supercapacitor cells, describing the charge and discharge behaviors by electrochemical parameters, such as equivalent series resistance, capacitance, and several electrode kinetic constants, seems more appropriate, in particular for electrochemical decomposition of the solvent.

In this paper, for fundamental understanding of supercapacitor charging and discharging behaviors, through experiment validation we present some simple mathematical models incorporating the voltage-independent parallel leakage process and electrochemical decomposition to describe the supercapacitor charge and discharge behaviors. Using these models, the experiment data could be simulated to obtain the desired values of parameters such as specific capacitance and equivalent series resistance from which both the energy and power density can be calculated. The simulated parameter values related to both parallel leakages and solvent decomposition could be used to predict supercapacitor's self-discharge and shelf-life, performance/efficiency losses, as well as the limiting workable cell voltage of the supercapacitors. Therefore, the proposed models are useful in evaluating and diagnosing supercapacitor cells. We hope these simple models could be used as a tool for understanding the charging–discharging behavior of the supercapacitors. Furthermore, we believe that these models could also be useful in obtaining the essential parameters of the supercapacitors such as equivalent series resistance and capacitance based on the recorded curves of charging–discharging.

2. Experimental

2.1. Electrode layer preparation

For electrode layer materials, Carbon black BP2000 (Cabot Corporation), conducting carbon Super C45 (from TIMCAL), and 60 wt% Polytetrafluoroethylene (PTFE)-water dispersion (Aldrich) were used as received without further modification.

For electrode layer preparation, the procedure has been described in our previous publication [3], and is repeated as below. Carbon and conducting carbon powders were first mixed with a Vortex Mixer (Thermo Scientific) for 30 min to form a uniformly-mixed powder, which was then transferred into a beaker containing both PTFE binder and ethanol solution under constant stirring to form a suspension. After the solvent was evaporated at high temperature, the paste formed was collected on a glass slide. This paste was manipulated by repeatedly folding and pressing using a spatula until a sufficient mechanical strength was achieved. Then this paste was rolled to a thin electrode sheet with the required thickness using a MTI rolling press. Finally, this electrode sheet was placed into a vacuum oven at 90 °C under active vacuum for at least 12 h. The formed dry electrode sheet was cut into two 2 × 2 square centimeters ($\mathrm{cm^2}$) for electrode layers, which were then sandwiched with a 30 μm thick porous PTFE separator (W. L. Gore & Associates, Inc.) in the middle, forming an electrode separator assembly (ESA). The assembly was then impregnated with an aqueous electrolyte containing 0.5 M Na_2SO_4 inside a vacuum oven at 60 °C for at least