



# Reversible heat of electric double-layer capacitors during galvanostatic charging and discharging cycles



Xinglei Zhang<sup>a</sup>, Wen Wang<sup>a,\*</sup>, Jun Lu<sup>a</sup>, Li Hua<sup>b</sup>, Jianpo Heng<sup>b</sup>

<sup>a</sup> School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>b</sup> Shanghai Aowei Technology Development Co., Ltd., Shanghai 201203, China

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## ABSTRACT

Heat generated in electric double-layer capacitors (EDLCs) during charging or discharging includes irreversible and reversible heat, the former is caused by the Joule effect, the latter is attributed to the ion adsorption/desorption at the electrode/electrolyte interface. In this study, the reversible heat of EDLCs is discussed with the surface Gibbs free energy at the electric double-layer, with the model the calculated temperature behaviors for the EDLCs with liquid electrolyte are compared with some experimental data. Temperature profiles and oscillation amplitudes in galvanostatic cycling which are affected by reversible and irreversible heats are discussed in detail. The relations of reversible heat with current as well as electrolyte temperature and concentration are analyzed as well.

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## 1. Introduction

Electric double-layer capacitors (EDLCs), also known as supercapacitor, have received much attention because of their remarkable characteristics, including fast charging/discharging, high power output, and long cycle life compared with conventional rechargeable batteries [1–4]. Supercapacitors are potential power source for electric and hybrid electric vehicles because they bridge the gap between traditional capacitors and rechargeable batteries. Thus far, supercapacitors have been used in braking energy recovery systems [5,6], energy storage devices for off-grid power generating systems combined with photovoltaic [7] and wind turbine power generation [8], and various power electronic devices [1,4].

In principle, a supercapacitor operates with heat generation and temperature rising, which mainly results from the Joule heating effect [9–11] and can be calculated with equivalent series resistance (ESR) [12]. ESR is related to the series connection of all resistance components and the internal contact resistance [13–15]. Once supercapacitors operate in high temperature environment, their ESR and lifetime expectancy gradually decrease, the self-discharge and aging rate increase [16–18]. Therefore, the temperature behavior for supercapacitor is important.

The experimental and theoretical studies about temperature behavior and thermal characteristic of supercapacitor have been

done in a couple of works [5,9–12,19–23]. Some of these previous works considered the Joule heat to be the unique heat source term [12,20,21], and then calculated the temperature fields during charging and discharging cycles. However, the calculation only considering Joule heat cannot explain the wave profile of experimental temperature during charging and discharging cycles.

Theoretically, the heat generated in supercapacitor includes both joule heat and reversible heat, which is resulted from the entropy change of ions in the electrolyte or the electrochemical reactions [5,9–11,22]. Dandeville et al. [10] obtained the heat profiles of symmetric supercapacitor with active carbon electrode with the calorimetric technique, and observed that the exothermic and endothermic processes were combined with the charging and the discharging respectively, then concluded that the reversible heat of  $K^+$  ions on the carbon surface was  $8.8 \text{ kJ mol}^{-1}$  at 1 V in aqueous electrolyte. According to the experiments on a supercapacitor with organic electrolyte, Pascot et al. [11] considered that the reversible heat effect was about 5%, and could be neglected. Schiffer et al. [9] noticed the oscillation of temperature profile in charging and discharging cycles and analyzed the chemical reaction and Peltier effect and entropy change for the reversible heat generation, moreover, the entropy change was considered leading to the reversible heat generation in a supercapacitor. Entropy change  $S$  and reversible heat generation rate  $\dot{Q}_{rev}$  could be displayed as below [9]:

$$S = 2\kappa_B \frac{CU}{e} \ln\left(\frac{V_H}{V_0}\right) \quad (1)$$

\* Corresponding author.

E-mail addresses: [wenwang@sjtu.edu.cn](mailto:wenwang@sjtu.edu.cn), [wangwen3250@hotmail.com](mailto:wangwen3250@hotmail.com) (W. Wang).

$$\dot{Q}_{rev} = -2 \frac{TK_B}{e} \ln\left(\frac{V_H}{V_0}\right) i(t) \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $C$ ,  $U$  and  $e$  are the capacitance and voltage of supercapacitor and the elementary charge,  $V_H$  and  $V_0$  denote the volumes in Helmholtz layer and total electrolyte, respectively. Here,  $\dot{Q}_{rev}$  is negative (releasing heat) when the transient current  $i(t)$  is positive during charging, and vice versa. The thermal behaviors of the supercapacitor were simulated in Refs. [5] and [24] under galvanostatic cycling on the basis of the above equations. The simulated results were in agreement with experimental data. However, the calculation demands  $V_H$  and  $V_0$ .

d'Entremont et al. [19,23] analyzed the temperature field of supercapacitor, and derived the reversible heat by considering the ion diffusion, steric effects, and the heat of mixing in EDLCs. The reversible heat generation rate  $\dot{q}_{rev}$  can be calculated as [19]:

$$\dot{q}_{rev} = \dot{q}_{E,d} + \dot{q}_{E,s} + \dot{q}_s \quad (3)$$

here,  $\dot{q}_{E,d}$  and  $\dot{q}_{E,s}$  are the heat generation rates correspond to the ion diffusion and steric effects, respectively,  $\dot{q}_s$  is attributed to the gradients of chemical potential, partial molar entropy, and temperature. Due to the reversible heat, the experimental temperature of supercapacitor has a certain wave characteristic [19]. However, the factors about the temperature oscillation were not discussed sufficiently. Analogously, P.M. Biesheuvel et al. [25] defined the reversible heat as negative Joule heating, and explained that when the current flowed down the potential gradient, the Joule heating was positive, whenever there was current flowed towards a high potential, it was negative.

d'Entremont et al. [26] proposed a simplified 1st-order thermal model for supercapacitors. The temperature  $T(t)$  was the sum of the irreversible temperature rise  $T_{irr}(t)$  and the reversible temperature oscillation  $T_{rev}(t)$  that referred to the Joule heat and reversible heat, respectively. The reversible temperature oscillation  $T_{rev}(t)$  can be calculated as below,

$$T_{rev}(t) = \begin{cases} \pm \frac{\alpha I_s}{C_{th}} (t - n_c t_c) & n_c t_c \leq t < (n_c + 0.5) t_c \\ \pm \frac{\alpha I_s}{C_{th}} [(n_c + 1) t - t] & (n_c + 0.5) t_c \leq t < (n_c + 1) t_c \end{cases} \quad (4)$$

$$\alpha = 2 \frac{C_{th} \Delta T_{rev}}{I_s t_c} \quad (5)$$

here,  $I_s$  is the current,  $C_{th}$  is the heat capacity,  $n_c$  is the number of charge and discharge cycles,  $t_c$  is the cycle period, the positive and negative signs correspond to the charging or discharging phase.  $\alpha$  is a semi-empirical parameter related to a certain supercapacitor.

The present study focus on the temperature behavior and the generated heat, deduces a reversible heat model about supercapacitor, the discussion on the reversible heat model will be helpful for understanding of the heat generation mechanism in EDLCs as well.

## 2. Discussion of reversible heat in EDLC

### 2.1. Assumption

In an EDLC, the electric energy is stored in the electric double layer (EDL), which is formed at the solid/liquid interface between electrode and electrolyte. Some positive and negative ions in the electrolyte are adsorbed at the negative and positive electrode surfaces to compensate for the electronic charge [1], respectively. Some ions are confined to agglomeration state from random motion, it results in energy release. During discharging, the adsorbed ions are desorbed from the EDL on the solid/liquid interface, and the extrication from the restriction on the

interface demands some energy. Therefore, heat is also combined with charging and discharging.

For analyzing the thermal performance of a supercapacitor, some assumptions are made as follows. (1) No chemical reaction occurs at the electrode/electrolyte interface, and the ion insertion into electrode is absent, just pure electrostatic adsorption or desorption of ions exists during charging or discharging. (2) The electrolyte used in the supercapacitor is binary and symmetric, the valences of cation and anion are  $z_+ = -z_- = z$ . (3) The electrolyte is homogeneous and ionized, and the specific heat capacity and thermal conductivity are constant during charging and discharging. (4) The supercapacitor capacitance is constant during charging and discharging cycles, and is not affected by temperature.

### 2.2. Mean activity of electrolyte solution

For the electrolyte solution, the activity  $a_i$  is considered as the effective concentration of the ion  $i$  [27],

$$a_i = \gamma_i \frac{m_i}{m^\ominus} \quad (6)$$

here,  $\gamma_i$  is the activity coefficient of ion,  $m_i$  is the molality of ion,  $m^\ominus$  is the standard molality, the molality  $m_i$  can be defined:

$$m_i = \frac{n_i}{m_{solvent}} \quad (7)$$

here,  $n_i$  denotes the amount of substance of ion species  $i$ , and  $m_{solvent}$  is the mass of solvent.

The molar number of ions  $n_{total} = n_0 + n$  in the EDL is related to the original molar number  $n_0 = v_i c_0 V_{EDL}$ , and the adsorbed ions  $n = 2C \times 0.5U/F$ , where  $v_i$ ,  $c_0$ , and  $F$  are stoichiometric coefficient of ion species  $i$ , original concentration, and the Faraday constant, respectively. The  $V_{EDL}$  is proportional to the surface area  $A$  and thickness of the EDL, both are related to the specific capacitance  $C_{dl}$  [1].

Consequently, the molality of ion  $i$  can be evaluated by

$$m_i = \frac{v_i c_0 F C \varepsilon_0 \varepsilon_r + C_{dl}^2 U C}{F \rho_{solvent} C \varepsilon_0 \varepsilon_r} \quad (8)$$

For the symmetric aqueous electrolyte solution, the mean ionic activity coefficient  $\gamma_{\pm}$  could be considered approximatively as the activity coefficient  $\gamma_i$  of positive or negative ion and can be obtained according to Pitzer theory [28–30]:

$$\ln \gamma_{\pm} = |z_+ z_-| f^\gamma + m \frac{2\nu_+ \nu_-}{\nu} B^\gamma + m^2 \frac{2(\nu_+ \nu_-)^{3/2}}{\nu} C^\gamma \quad (9)$$

where,  $\nu = \nu_+ + \nu_-$ , and  $\nu_+ = \nu_-$  for symmetric electrolyte.  $f^\gamma$ ,  $B^\gamma$ , and  $C^\gamma$  are Pitzer fitting parameters, the involved parameters at 25 °C had been listed in Ref. [28,30].

For the organic electrolyte, the ionic activity coefficient  $\gamma_i$  of ion can be expressed as below according to the Debye-Hückel limiting law for binary and symmetric organic electrolyte [19],

$$\ln \gamma_i = - \frac{z^3 e F^2 (c_1 + c_2)^{1/2}}{8 \pi (\varepsilon_0 \varepsilon_r R T)^{3/2}} \quad (10)$$

### 2.3. Energy conservation equation

During charging, electric energy is stored in the EDL, during discharging, some electric energy is released, and some of them convert into the Joule heat. On the basis of the energy conservation, the relation between the variation of Gibbs free energy  $\Delta G$  and the electric energy is:

$$dG = dQ - znFdE \quad (11)$$

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