Journal of Power Sources 374 (2018) 257–268

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Isothermal calorimeter for measurements of time-dependent heat generation rate in individual supercapacitor electrodes

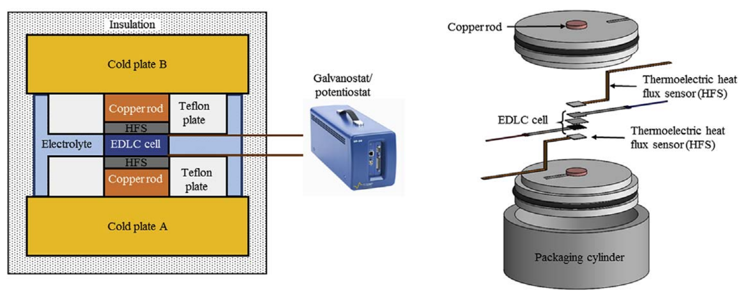
Obaidallah Munteshari[a,b], Jonathan Lau[c], Atindra Krishnan[a], Bruce Dunn[c], Laurent Pilon[a,*]

[a] Mechanical and Aerospace Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, Los Angeles, CA 90095, USA
[b] Mechanical Engineering Department, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran 31261, Saudi Arabia
[c] Materials Science and Engineering Department, Henry Samueli School of Engineering and Applied Science, University of California, Los Angeles, CA 90095, USA

HIGHLIGHTS

- An isothermal calorimeter was designed, manufactured, and carefully validated.
- The device can measure heat generation rate at each electrode of supercapacitors.
- Its capabilities were illustrated with EDLC electrodes and various electrolytes.
- Irreversible heat generation rate was due to Joule heating.
- Reversible heat generation rate was significantly lower at the negative electrodes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Isothermal calorimeter
Energy storage
Pseudocapacitors
Supercapacitors
Thermal management
Heat generation

ABSTRACT

Heat generation in electric double layer capacitors (EDLCs) may lead to temperature rise and reduce their lifetime and performance. This study aims to measure the time-dependent heat generation rate in individual carbon electrode of EDLCs under various charging conditions. First, the design, fabrication, and validation of an isothermal calorimeter are presented. The calorimeter consisted of two thermoelectric heat flux sensors connected to a data acquisition system, two identical and cold plates fed with a circulating coolant, and an electrochemical test section connected to a potentiostat/galvanostat system. The EDLC cells consisted of two identical activated carbon electrodes and a separator immersed in an electrolyte. Measurements were performed on three cells with different electrolytes under galvanostatic cycling for different current density and polarity. The measured time-averaged irreversible heat generation rate was in excellent agreement with predictions for Joule heating. The reversible heat generation rate in the positive electrode was exothermic during charging and endothermic during discharging. By contrast, the negative electrode featured both exothermic and endothermic heat generation during both charging and discharging. The results of this study can be used to validate existing thermal models, to develop thermal management strategies, and to gain insight into physicochemical phenomena taking place during operation.

1. Introduction

Electric double layer capacitors (EDLCs) have attracted significant interest as energy storage systems thanks to their large power densities, long cycle life, and high cycle efficiency compared with batteries [1,2]. They are attractive for many applications requiring rapid charging/discharging, such as regenerative braking in hybrid or electric vehicles and renewable energy harvesting systems [2–7]. EDLC devices consist of two carbon-based electrodes and a separator immersed in aqueous or organic electrolytes. They store electric charges in the electric double

* Corresponding author.
E-mail address: pilon@seas.ucla.edu (L. Pilon).

https://doi.org/10.1016/j.jpowsour.2017.11.012
Received 18 August 2017; Received in revised form 2 October 2017; Accepted 4 November 2017
Available online 25 November 2017
0378-7753/

Nomenclature

A	Footprint area of the heat flux sensor, cm^2
c_p	Specific heat, J/(kg·°C)
C_g	Gravimetric capacitance, F/g
I	Current, mA
k	Thermal conductivity, W/(m·°C)
L	Electrode thickness, cm
m	Mass loading of active material in electrode, mg/cm^2
n	Cycle number, -
q	Heat flux, mW/cm^2
$\dot{q}$	Volumetric heat generation rate, mW/cm^3
$\dot{Q}$	Heat generation rate, mW
$\bar{\dot{Q}}$	Time-averaged heat generation rate, mW
R_i	Electric resistance of resistor or electrode "i", Ω
R_s	Internal resistance for entire EDLC device, Ω
S	Heat flux sensor sensitivity, μV/(W/m^2)
S_o	Heat flux sensor sensitivity at 22.5 °C, μV/(mW/cm^2)
S_c	Heat flux correction factor, μV/[°C·(mW/cm^2)]
t	Time, s
t_c^-	Time immediately after the beginning of the discharging step, s
t_c^+	Time at the end of the charging step, s
T_c	Cold plate temperature, °C
T_o	Operating temperature, °C
ΔV	Voltage difference generated in the heat flux sensor, μV

Greek symbols

ν	Scan rate, mV/s
ψ_s	Potential across an EDLC cell, V

Superscripts and subscripts

A or B	Refers to heat flux sensor A or B
c	Refers to charging step
cd	Refers to charging-discharging cycle
d	Refers to discharging step
J	Refers to Joule heating
$J, 1$ or $J, 2$	Refers to Joule heating in Resistor 1 or 2
max	Refers to maximum
min	Refers to minimum
T	Refers to entire cell
rev, i	Refers to reversible in electrode "i"
+ or −	Refers to positive or negative electrode

layer (EDL) forming at the mesoporous electrode/electrolyte interfaces.

EDLCs are usually cycled at high current densities resulting in significant amount of volumetric heat generation. This, in turn, can result in excessive temperature rise during normal operation leading to (i) accelerated cell aging [3,4,8–11], (ii) increased self-discharge rates [3,8–10], and possibly (iii) electrolyte decomposition and evaporation [10,12]. Heat generation in EDLCs can be attributed to irreversible and reversible processes. Irreversible heat generation has been shown to correspond to Joule heating [2,8,13–16]. It is proportional to the square of the current and, as such, is always positive. It remains constant throughout the cell under constant current cycling [15–18]. On the other hand, recent physical modeling indicates that reversible heat generation is affected by ion diffusion, steric effects, entropy of mixing, and possible redox reactions [16,18]. It occurs mostly near the electrolyte/electrode interface where the EDL forms [16]. The amount of reversible heat generated in the device during a charging step under constant current cycling has been found, both experimentally [8,15] and theoretically [8,16,17], to be proportional to the current.

The present study aims to measure the instantaneous heat generation rates in each electrode of EDLC devices under galvanostatic cycling in order to improve our understanding of the responsible physiochemical phenomena. To do so, an isothermal calorimeter was designed, assembled, and validated to measure the time-dependent irreversible and reversible heat generation rates in each electrode of electrochemical cells. Several EDLC devices consisting of two identical electrodes made of activated carbon and different aqueous or organic electrolytes were investigated. The results will be instrumental in validating and/or improving existing thermal models and in developing thermal management strategies. They can also be used to give insight in the physicochemical processes involved in charging and discharging of electrochemical energy storage systems.

2. Background

2.1. Thermal models

Several thermal models of EDLCs have been proposed in the literature [3,8–10,15–19]. Most of them aimed to predict the temperature distribution within a cell by solving the energy equation considering Joule heating as the only source of heat generation. By contrast, Schiffer et al. [8] developed a thermal model accounting for reversible heat generation rate through an ad hoc model based on entropy change considerations and experimental observations [8]. Their model assumed that the reversible heat generation rate was proportional to the current [8].

More recently, d'Entremont and Pilon [16] developed a spatiotemporal physical model based on first principles by coupling the heat diffusion equation with the modified Poisson-Nernst-Planck (MPNP) model to derive analytical expressions for both irreversible and reversible heat generation rates in EDLCs. The irreversible heat generation rate was attributed solely to Joule heating. By contrast, the reversible heat generation rate was attributed to diffusion, steric effects, and entropy changes [16]. Numerical simulations of the heat generation rate in a binary and symmetric electrolyte were performed for planar electrodes during constant current cycling. First, the irreversible heat generation rate was found to be proportional to the square of the imposed current I^2. On the other hand, the time-averaged reversible heat generation rate was exothermic during charging and endothermic during discharging and proportional to the imposed current [16]. These results were in qualitative agreement with experimental data reported in the literature [8,19].

D'Entremont and Pilon [17] extended their physical model for heat generation rate in EDLCs to electrolytes consisting of multiple and/or asymmetric ion species with arbitrary ion diameter and diffusion coefficient. They observed that dissimilarity in ion valency, diameter, and/or diffusion coefficient between cations and anions of the electrolyte resulted in different heat generation rates at the two electrodes of EDLC devices [17]. In fact, larger ion valency and/or diffusion coefficient led to smaller irreversible heat generation rate due to an increase in electrolyte electrical conductivity [17]. In addition, the total reversible heat generation rate during charging was larger for smaller ion diameter and/or larger valency [17]. Additionally, d'Entremont and Pilon [18] further extended their model to hybrid pseudocapacitors to account for both electric double layer (EDL) formation and faradaic reactions in the pseudocapacitive electrode. First, carbon electrode exhibited the same thermal behavior observed in EDLC carbon electrodes [16,18]. Second, two regimes of operation were observed at the pseudocapacitive electrode namely a faradaic and a capacitive regime [18]. The faradaic regime occurred at low current densities and slow charging/discharging when the heat generation rate associated with