Measuring time-dependent heat profiles of aqueous electrochemical capacitors under cycling

Y. Dandeville, Ph. Guillemet, Y. Scudeller*, O. Crosnier, L. Athouel, Th. Brousse

University of Nantes, Ecole Polytechnique, LGMPA, La Chantrerie, rue Christian Pauc, BP 50609, 44306 Nantes Cedex 03, France

ARTICLE INFO

ABSTRACT

A calorimetric technique was developed for determining time-dependant heat profiles of electrochemical capacitors. The profiles were extracted from the temperature change of the capacitor during charge–discharge current cycles. The technique is described and its good performance is demonstrated. Experiments were carried out on symmetric and asymmetric aqueous capacitors prepared with activated carbon and manganese oxide as active materials. Heat in double-layer and hybrid capacitors, C–C and C–MnO$_2$, varied with time, according to special profiles depending on storage processes. In carbon double-layer capacitors, the heat component was decomposed into a reversible and an irreversible term. Results suggested that irreversible heat was caused by the Joule loss through the porous structure and the reversible heat by the ion adsorption on the carbon surface. Moreover, endothermic and exothermic processes were observed on the MnO$_2$ electrode of the asymmetric capacitor, over the charge and the discharge respectively, proportional to the charge rate. These results suggested that heat in the MnO$_2$ electrode originated from the redox reactions and ion adsorption on the active material.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical capacitors, also known as supercapacitors, are promising energy storage devices intermediate between rechargeable batteries and electrolytic capacitors with respect to energy and power performance [1–3]. They are attractive over a wide range of applications as back-up memory for electronic devices, peak power assistance to reduce the duty-cycle on a battery, and as the temporary energy storage in electric vehicles [1–3]. Schematic of a capacitor cell is shown in Fig. 1. The cell consists of two porous electrodes, coated on metal current collectors and a polymer separator placed between them wetted with a liquid electrolyte. Electrochemical capacitors can be classified into two types depending on the charge processes involved: electric double-layer capacitors (EDLC) and pseudo-capacitors. In EDLCs, the charge process is electrostatic whereas in pseudo-capacitors redox reactions are involved [1]. EDLCs have a symmetric design, as represented in Fig. 1, where charges are stored at the two electrodes formed with high-surface-area porous carbon. The charge is stored at the surface of the carbon through electrostatic interactions in the electrochemical-double-layer between the carbon surface and the electrolyte. Otherwise, an asymmetric design of cell shown in Fig. 1

can be considered. It combines a faradic positive electrode, prepared with a metal oxide as active material for instance, with an EDLC negative electrode prepared with activated carbon. Asymmetric cells can substantially improve the energy density [3,4]. Nowadays, manganese dioxide MnO$_2$, is an attractive active material for the positive electrode which is suitable for an increase in energy performance of electrochemical capacitors [4,5]. Moreover MnO$_2$ offers a real potential for applications because of its low cost and environmental friendly nature.

While applying a current cycle, electrochemical capacitors produce heat that cause temperature changes and drastically reduce performance in terms of reliability, capacity and time response, thus impacting the way the device works in electrical circuits [1,6,7]. Furthermore, heat remains one of the key factors affecting safety. In addition, heat data is needed as well for predicting the operating temperature and the energy efficiency while varying the current, and as such, understanding the ageing mechanisms under operation. Generally, predicting heat in electrochemical capacitors has not been done. Indeed, these devices operate with complex interplay of chemical reactions, charge processes, combined with heat and mass transport [8]. In electrochemical capacitors, heat is generated in the volume of the active materials and the electrolyte, with a rate depending on the cycle profile and charge mechanisms involved. Heat results from Joule losses, cell polarization and reversible entropy change coming from the chemical and ionic bonds formed during the processes [8,9]. Joule losses result from

---

* Corresponding author.
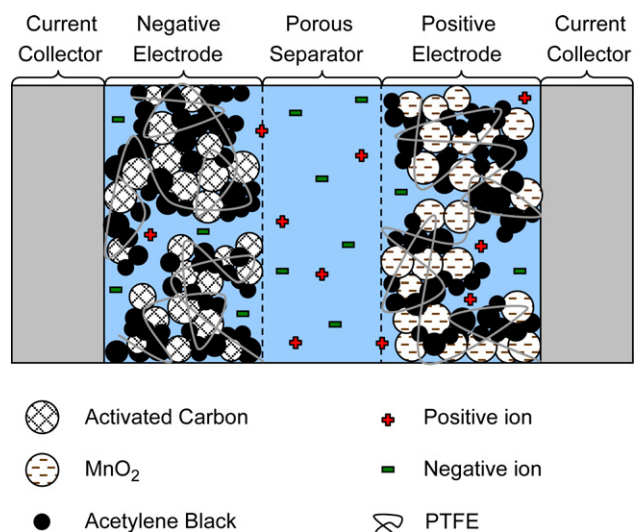*E-mail address:* yves.scudeller@univ-nantes.fr (Y. Scudeller).

Fig. 1. Electrochemical capacitors investigated in the present work. Heat is generated in the volume of each component of the cell. Heat varies with time according to profiles depending on current cycles applied. The symmetric double layer capacitor cell consists of two identical activated carbon electrodes separated with a porous separator wetted with an electrolyte. The asymmetric capacitor cell, represented here, combines one non-faradic electrode with a faradic electrode prepared with manganese dioxide as active material. Energy storage in the bulk of the faradic electrode (MnO_2) involves redox reactions.
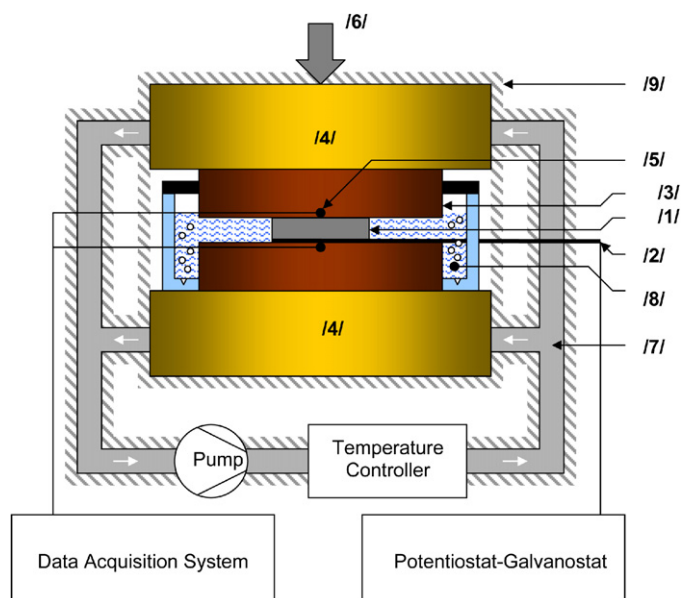

Fig. 2. Schematic of the calorimeter: (1) Electrochemical cell under test, (2) current collectors, (3) heat-flux sensor, (4) cold plate, (5) thermocouples, (6) force sensor 0–$200\,kg\,cm^{-2}$, (7) cooling fluid, (8) electrolyte bath bubbled with nitrogen, and (9) thermal insulation.

the charge transport across the resistive paths of the solid skeleton and the liquid electrolyte confined in the pores of the materials. Moreover, in pseudo-capacitors, other reversible and irreversible heat effects take place at the interface between the electrolyte and the active material [8,9]. Reversible heat can be associated with ion adsorption and electrochemical reaction on the active materials. Moreover, in faradic systems, polarization heat can occur in the electrodes. The polarization heat results from irreversible processes (oxidation and intercalation of ions) depending on the difference between the electrode potential and the open circuit potential [8,9,16,17]. Polarization heat can be regarded similarly as the Joule effect. Generally, heat generated in electrochemical capacitors varies with time due to the time-dependent charge processes.

Calorimetric techniques offer a direct route for determining heat in energy storage devices such as rechargeable batteries, dielectric capacitors, and electrochemical capacitors [10–14]. Those techniques are suitable for exploring the heat effects during the charge storage processes, thus contributing to a better understanding of mechanisms involved. On this topic, DC and AC calorimetric techniques have already been employed to investigate a wide variety of electrochemical systems. Thus, Peltier heat has been studied for different electrochemical processes such as the Hydrogen electrode reaction in the LiCl-KCl-LiH system [15], Ag deposition and dissolution [14], aluminium electrolysis [16] the reaction between polypyrrole and electrolyte [17].

This paper presents a calorimetric technique for measuring the time-dependant heat profiles of electrochemical capacitors while applying current cycles. The technique is presented and the performance demonstrated. Experiments were carried out on symmetric and asymmetric capacitors prepared with porous carbon and manganese oxide in an aqueous electrolyte. Time-dependant heat profiles of carbon–carbon and carbon–MnO_2 capacitors were determined versus the current. Then, the Peltier coefficients between the active materials and the electrolyte have been derived from the heat profiles on both the carbon and MnO_2 electrode. The results are reported and discussed here.

2. Experimental technique

Preliminary tests revealed that temperature of the supercapacitor cells oscillated with a large amplitude while cycling depending on the charge current and cycle frequency (see Section 3). These tests indicated that heat generated in capacitors could substantially vary with time in the course of the charge and the discharge. Moreover, temperature oscillations in double-layer capacitors have been already reported by different authors, in acetonitrile [18], and propylene carbonate $1\,M\,-N(C_2H_5)4BF_4$ electrolytes [10]. Otherwise, it is recognized that the electrode reactions taking place in the pseudo-capacitors cause substantial temperature change [11–14].

2.1. Calorimeter

A heat conduction calorimeter has been designed to determine the time-dependant heat profiles of electrochemical capacitors exposed to different charge–discharge conditions in current, voltage, and temperature. A first apparatus has already been constructed for measuring average heat in EDLCs [10]. The apparatus developed here offers higher performance for dynamic measurements with a good stability and precision in temperature. Materials were chosen for carrying out tests for several hours over a wide temperature range between $-20\,°C$ and $+100\,°C$. A schematic of the calorimeter is given in Fig. 2. The cell under test /1/ was assembled and pressed between two twin plates in polyphenylene sulfide (PPS) attached to a cold plate /3/ symmetrically positioned to form a heat-flow sensor as shown in Fig. 2. The cold plate was kept at constant temperature with a fluid circulator controlled in temperature. The heat-flow sensor delivered a voltage proportional to the temperature difference between the cell and the cold plate with a sensitivity of $630\,\mu V/°C$ between $-20\,°C$ and $+120\,°C$. As indicated in Fig. 3, the PPS plates of 20 mm thickness and 80 mm diameter, incorporated 16 thermocouples connected in series (8 per plate) of $100\,\mu m$ diameter, in contact with the cell. The cold junctions of the thermocouples were attached on the cold plate. The hot junctions were in contact with the electrochemical cell, as shown in Fig. 3. The cold and hot junctions were electrically insulated from