Journal of Power Sources 303 (2016) 294–304

Contents lists available at ScienceDirect

Journal of Power Sources

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

A systematical evaluation of polynomial based equivalent circuit model for charge redistribution dominated self-discharge process in supercapacitors

Ji-Fu Shen [a], Yi-Jun He [a, *], Zi-Feng Ma [a, b]

[a] Department of Chemical Engineering, Shanghai Electrochemical Energy Devices Research Center, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Sinopoly Battery Research Center, Shanghai 200241, China

HIGHLIGHTS

- Investigate the effects of initial voltage and temperature on charge redistribution dominated self-discharge.
- Establish a polynomial based equivalent circuit model.
- Systematically evaluate the effect of polynomial order on model performance.
- Investigate the impacts of initial voltage and temperature on model performance.
- Compare the prediction performance between polynomial and interpolation methods.

ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form
7 October 2015
Accepted 1 November 2015
Available online 14 November 2015

Keywords:
Supercapacitor
Charge redistribution
Self-discharge
Equivalent circuit model
Polynomial model

ABSTRACT

Accurate modeling of the charge redistribution dominated self-discharge process plays a significant role in power management systems for supercapacitors. Although equivalent circuit models (ECMs) are widely used to describe the nonlinear behaviors of the self-discharge process, they are usually separately established at different initial voltages, which might result in poor prediction performances at other unseen initial voltages. In this study, a three-branch model with a leakage resistance is used to describe the nonlinear dynamic behavior of the supercapacitor self-discharge dominated by charge redistribution and the circuit parameters in ECMs are explicitly modeled as a function of the initial voltage. Polynomial functions with different orders are systematically evaluated by means of fitting and prediction accuracy. The impacts of initial voltage and temperature on the charge redistribution dominated self-discharge process are experimentally investigated with a 3000 F commercial supercapacitor. The modeling results show that a 5th-order polynomial function is sufficient high enough to characterize the nonlinear effect of initial voltage on the charge redistribution dominated self-discharge in terms of prediction accuracy. Moreover, the prediction accuracy of polynomial function based ECMs are significantly better than that of interpolation based ECMs, which further validates the effectiveness of the proposed model.

1. Introduction

Supercapacitors, consisting of two high-surface area electrodes separated by an electrolyte layer, have been increasingly used in wireless sensor networks [1–4], electric and hybrid vehicles [5–7], wind/solar energy generation system [8,9], etc. Compared to batteries, supercapacitors often have higher specific power density and longer cycle life, but offer low specific energy density [10]. Recently, hybrid energy storage systems consisting of supercapacitor and lithium-ion batteries have attracted significant attention in the field of electric vehicles and wind/solar energy generation system for meeting the relatively high peak-to-average power requirement [11–14]. Commercial applications of supercapacitors often require power management systems to safe and reliable operation of supercapacitors [3,11]. Since a fast self-discharge in supercapacitors could results in charge/energy loss and voltage drop, it is important to give a thorough understanding of the self-discharge dynamic behavior and develop an accurate

* Corresponding author.
E-mail address: heyijun@sjtu.edu.cn (Y.-J. He).

http://dx.doi.org/10.1016/j.jpowsour.2015.11.001
0378-7753/

terminal voltage prediction model for optimal designing power management systems [2,4].

Mathematical modeling provides a promising approach to reveal the nonlinear behavior of charging/discharging, charge redistribution and self-discharge processes in supercapacitors [15,16], which can be broadly classified into first-principle electrochemical models [17], data-driven empirical models [18,19] and equivalent circuit models (ECMs) [1–4,20–24]. The electrochemical models, described as partial differential equations (PDEs), usually have high computational complexity, which cannot meet the requirement of online applications. Although the data-driven empirical models are relatively easy to establish by means of input–output measurement data, they are often difficult to capture the underlying dynamic mechanisms of supercapacitors and the extrapolation accuracy of empirical models cannot be guaranteed. Compared to electrochemical models and empirical models, ECMs have the advantages of relatively fast computation and high extrapolation accuracy, and have been attracted significant attention in power management systems [23]. ECMs can be established either in frequency domain by electrochemical impedance spectroscopy (EIS) measurements [20–22] or in time domain by constant power/current tests [1–4,23,24]. EIS is often used in an offline manner and is relatively expensive, which limits it on-board applications. This study will focus on constructing an ECM in time domain for describing the self-discharge dynamics of supercapacitors.

It has been widely recognized that the self-discharge process is mainly ascribed to three mechanisms: activation-controlled Faradaic process, diffusion-controlled Faradaic redox reactions and internal ohmic leakage [1,2,25–28]. Since activation-controlled Faradaic process can only occur if the supercapacitor is overcharged, the diffusion-controlled process and the internal ohmic leakage need to be considered for normal operation of the supercapacitor [27]. Note that the diffusion-controlled process and the internal ohmic leakage are of different time scales, where the former only dominates the self-discharge in the first few hours and the latter usually dominates the self-discharge during the whole resting time [1,2,25,27]. For accurately description of the nonlinear self-discharge process with multi scale characteristics, an ECM with three RC branches and a leakage resistance has been developed [27]. Furthermore, a novel ECM with two RC branches and a variable leakage resistance (VLR) has been proposed, in which two RC branches with different time constants to characterize the charging-redistribution process and the VLR to characterize the self-discharge process [1–3]. The VLR has been first represented as a function of the self-discharge time, and then modified as a function of the supercapacitor terminal voltage, which is more suitable for practical application. Although it has been realized that the model circuit parameters (e.g. capacitance and resistance) are dependent on operation conditions such as initial voltage and temperature [1,2,27], none of the developed ECMs explicitly includes the initial voltage effect in the modeling of the supercapacitor self-discharge process, which might result in inaccuracy terminal voltage prediction for unseen initial voltage. Therefore, we will explicitly model the circuit parameters as a function of initial voltage and systematically investigate the effect of polynomial order on the fitting and prediction accuracy of ECMs. In addition, the prediction performances of proposed polynomial function based ECMs and cubic spline interpolation based ECMs are compared. To the best of our knowledge, this study is the first attempt to propose a polynomial model with inclusion of initial voltage for the supercapacitor charge redistribution dominated self-discharge process, and give a systematic evaluation of polynomial order.

The remainder of this paper is structured as follows. The ECM of the charge redistribution dominated self-discharge process is first described. Then, the parameter estimation procedure is presented. The effectiveness of the proposed model is next validated by experimental data. Finally, conclusions and future research directions are provided.

2. Polynomial based equivalent circuit model of supercapacitors

For detailed description of the nonlinear behavior of charge redistribution dominated self-discharge process in supercapacitor, a three-branch model with a leakage resistance is adopted and shown in Fig. 1. Each branch consists of a resistance and capacitance. The first, second and third branches determine the short-term voltage evolution during charge and discharge cycles, the medium-term and long-term charge redistribution, respectively [2,23,29]. The physical meaning of a three branches model can also be interpreted as ion mobility within three groups of pore sizes (i.e. macro, meso and micro), in which the first, second and third branches are corresponding to macro-, meso- and micro-pores respectively [15]. In general, the macro-pores have much smaller time constants than the meso- and micro-pores. These three branches with different time scales will show different response characteristics to the charging/discharging, charge redistribution and self-discharge processes. Generally, the time constant of the first branch is significantly smaller than that of the second and third branches. In the charging phase, all the current is assumed to be mainly injected to the first branch, while during the charge redistribution and self-discharge phase, part of the charge stored in the first branch will be redistributed to the second and third branches and self-discharged through the leakage resistance. Hence, the established three-branch model can be able to predict various nonlinear behaviors of the supercapacitors such as charging/discharging, charge redistribution and self-discharge. In addition, in this study, the circuit parameters of the first branch are first separately determined using a charging curve, and the remaining circuit parameters are then determined using the self-discharge curves.

2.1. Modeling charging process

For the first branch, a differential capacitance C_1 shown in Eq. (1) is often used to characterize the nonlinear behavior of the immediate capacitance.

$$C_1 = C_0 + K_V \times V_1 \tag{1}$$

where C_0 and $K_V \times V_1$ denote a constant capacitance and a linear

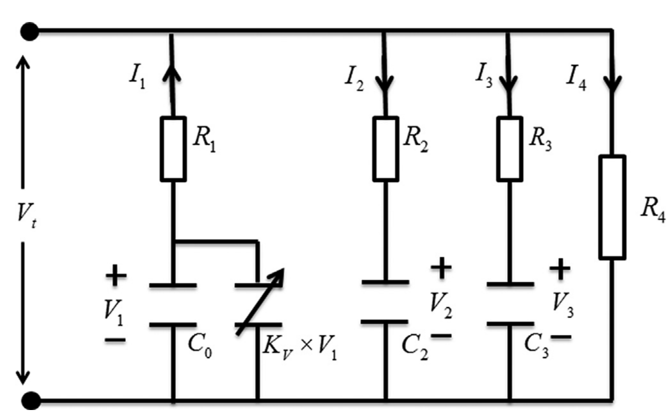

Fig. 1. Three-branch model with a leakage resistance for self-discharge process.