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Bivariate quadratic method in quantifying the differential capacitance and energy capacity of supercapacitors under high current operation

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HIGHLIGHTS

- A bivariate quadratic method for the electrical characteristics of supercapacitors.
- The capacitance and energy capacity are derived directly from terminal measurements.
- The capacitance–voltage characteristic is more complex than a linear function.
- The capacitance exhibits variation between charging and discharging states.
- Up to 79% of the total energy is available within the 50%–100% nominal voltage range.

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ABSTRACT

Capacitance and resistance are the fundamental electrical parameters used to evaluate the electrical characteristics of a supercapacitor, namely the dynamic voltage response, energy capacity, state of charge and health condition. In the British Standards EN62391 and EN62576, the constant capacitance method can be further improved with a differential capacitance that more accurately describes the dynamic voltage response of supercapacitors. This paper presents a novel bivariate quadratic based method to model the dynamic voltage response of supercapacitors under high current charge–discharge cycling, and to enable the derivation of the differential capacitance and energy capacity directly from terminal measurements, i.e. voltage and current, rather than from multiple pulsed-current or excitation signal tests across different bias levels. The estimation results the author achieves are in close agreement with experimental measurements, within a relative error of 0.2%, at various high current levels (25–200 A), more accurate than the constant capacitance method (4–7%). The archival value of this paper is the introduction of an improved quantification method for the electrical characteristics of supercapacitors, and the disclosure of the distinct properties of supercapacitors: the nonlinear capacitance–voltage characteristic, capacitance variation between charging and discharging, and distribution of energy capacity across the operating voltage window.

1. Introduction

In the electrical modelling of supercapacitors, capacitance and resistance are the fundamental electrical parameters used to evaluate the electrical characteristics of a supercapacitor, namely the dynamic voltage response, energy capacity, energy loss, state of charge and health condition. The capacitance of supercapacitors (electrochemical capacitors) consists of two main charge storage principles: double-layer capacitance and pseudocapacitance [1,2], depending on the electrode material used. In double-layer capacitance, charge is stored electrostatically in the interface between an electrode and an electrolyte. When an external voltage is applied on one electrode, the counter-ions of the electrolyte are attracted to the surface of the electrode, forming two layers of charge that separated by a molecular dielectric layer (mono-layer of solvent molecules) at the electrode–electrolyte interface. In pseudocapacitance, the storage mechanism is a reversible Faradaic charge-transfer process, achieved by the adhesion of electrolyte ions onto the surface of electrode (made up of metal oxides or conducting polymers) via electrosorption, intercalation or reduction–oxidation reactions.

The capacitance of a supercapacitor is susceptible to changes in operating conditions such as voltage, frequency, temperature, and charge propagation [3–5], mainly related to the mobility of charge

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during operation. The voltage dependency of the device capacitance can be explained by the effect of the applied electric field on the permittivity of the molecular dielectric, the separation of the charge layer and the molarity of electrolyte. Besides, the capacitance is proportional to the effective area of the charge layer that formed at the electrode–electrolyte interface during operation, not the total surface area of typically highly porous electrode. This effective area depends on the accessibility of electrode pores and the propagation of electrolyte ions into the different pore depths/sizes of electrode. The propagation of ions takes longer time to reach long narrow pores than short wide pores, hence resulting in higher capacitance (due to larger effective area) at lower frequency operation. This explains both the charge and frequency effects on the capacitance.

In the British Standards EN62391 [6] and EN62576 [7] (identical to IEC62391 and IEC62576), the capacitance of supercapacitors is quantified as a constant capacitance by using the constant current discharge test method, without considering the voltage and charge dependencies of the supercapacitor. This constant capacitance based identification method is found to be inadequate to precisely represent the dynamic terminal behaviour of supercapacitors [8–10].

The term differential capacitance is the measurement of capacitance as a function of voltage. Differential capacitance is commonly introduced within the electrical models of supercapacitor to describe the voltage dependency of capacitance. In the deployment of differential capacitance in various resistor–capacitor equivalent circuit models, the main challenge is obviously to accurately establish the relationship of capacitance versus voltage, which can be identified from either the frequency response to a small excitation signal (typically currents of a few mA), e.g. in tests using electrochemical impedance spectroscopy (EIS) [4,11], or the voltage response to a controlled pulse-current (in tens of Amperes) in studies using the constant current test method [12–14] repeatedly across different bias levels. The differential capacitance can then be modelled as a linear function [4,12,14–16], a quadratic function [11], or even a quartic function [17]. The order of function relates to the size of the experimental dataset (number of bias levels) used in defining the relationship of capacitance versus voltage. Studies with small datasets consume less experimental time and generally allow simple analysis compared to studies with large datasets; however the precision of modelling could be comprised.

Apart from the linear capacitance–voltage based equivalent circuit models, several analytical models have been proposed to model the dynamic behaviour of supercapacitors. These models are ladder network model with a complex pore impedance block [18], transmission line model with the hybridisation of temporal and frequency approaches [11], artificial neural network based models [19–21], and fractional non-linear model [22]. In these models, the parameters identification often involves intensive experimentation and computation to achieve good approximation results.

This paper presents a highly accurate and practical method to model the dynamic voltage response, and quantify the differential capacitance and energy capacity of supercapacitors under high current operations (up to 200 A) that typically experienced in real-life applications. A bivariate quadratic function is developed and applied for the first time to represent the dynamic charge–voltage characteristic of supercapacitors. This proposed method allows the differential capacitance and energy capacity of supercapacitors to be derived directly from the terminal measurements, i.e. voltage and current, rather than from multiple pulse-current or excitation signal tests at different bias levels as discussed previously. Hence, the bivariate quadratic based method can eliminate the trade-off between accuracy and practicality (i.e. simplicity of testing) in identifying the capacitance–voltage characteristic for the electrical modelling of supercapacitors.

2. Experimental

This study aims to understand the dynamic behaviour of supercapacitors during the high power/current operations often experienced in real-life applications. In the laboratory, these operating conditions are recreated as constant current charging–discharging experiments by using a programmable high current test system. The high current test system [10] developed by the authors, supports three types of charge/discharge/cycling current profile – constant current, sinusoidal current, and customised current cycles, at current levels up to 250 A. A data acquisition device, based on a National Instrument USB-6218, is deployed to record the voltage, current and temperature measurements of the supercapacitor under test.

High current charging–discharging experiments were conducted on Maxwell's Boostcap supercapacitors. The specifications of these double-layer based supercapacitors are an equivalent series resistance (ESR) of 0.8 mΩ, a nominal capacitance of 650 F, and a rated voltage of 2.7 V. From a constant current charging–discharging experiment of 200 A, the voltage response of a 650 F supercapacitor cell operated between 0 and 2.7 V is as depicted in Fig. 1. The current signal is the effective square wave, with a corresponding triangular voltage response. The 'charge' currents are represented by negative values whilst the 'discharge' currents are represented by positive values. Both the voltage and current time series data are subsequently used as the input data for the proposed numerical method, described in following section.

3. Bivariate quadratic method

3.1. Simple resistor–capacitor circuit

For practical purposes, a simple series resistor–capacitor (RC) equivalent circuit is applied to represent the dynamic voltage response of supercapacitors during fast charging–discharging. The circuit parameters are stated as the equivalent series resistance (ESR) and differential capacitance, as shown in Fig. 2. In terms of circuit notation, the terminal voltage of the supercapacitor is denoted as V_{SC}, the current of the supercapacitor as I_{SC}, the voltage across the ESR as V_R, and the differential capacitor voltage is V_C.

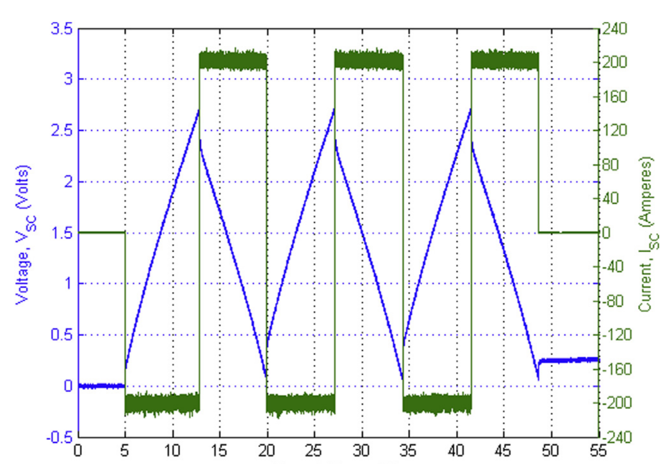

Fig. 1. The voltage response of a supercapacitor under charge–discharge cycling at 200 A.