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Low-order mathematical modelling of electric double layer supercapacitors using spectral methods

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HIGHLIGHTS

- Low-order, physics based electric double layer supercapacitor models simulated.
- Spectral element method used for spatial discretisation.
- Compared to finite difference methods spectral element increases solution accuracy.
- Dependence of ionic concentration on conductivity is modelled.
- Model captures frequency dependence of capacitance.

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ABSTRACT

This work investigates two physics-based models that simulate the non-linear partial differential algebraic equations describing an electric double layer supercapacitor. In one model the linear dependence between electrolyte concentration and conductivity is accounted for, while in the other model it is not. A spectral element method is used to discretise the model equations and it is found that the error convergence rate with respect to the number of elements is faster compared to a finite difference method. The increased accuracy of the spectral element approach means that, for a similar level of solution accuracy, the model simulation computing time is approximately 50% of that of the finite difference method. This suggests that the spectral element model could be used for control and state estimation purposes. For a typical supercapacitor charging profile, the numerical solutions from both models closely match experimental voltage and current data. However, when the electrolyte is dilute or where there is a long charging time, a noticeable difference between the numerical solutions of the two models is observed. Electrical impedance spectroscopy simulations show that the capacitance of the two models rapidly decreases when the frequency of the perturbation current exceeds an upper threshold.

1. Introduction

This paper develops a new spectral element implementation of two non-linear models that describe the behaviour of an electric double layer supercapacitor. Supercapacitors are electrical energy storage devices for high-power applications [1,2]. In contrast to conventional dielectric capacitors, supercapacitors store their energy using the electric double layer (EDL) phenomenon with high specific surface area electrodes. Storing energy in this manner increases the energy density, while still retaining the inherently high power density characteristic of capacitors.

Supercapacitors have been successfully implemented in a range of applications including grid stabilisation [3] and hybrid electric vehicle power systems [4]. The growing popularity of supercapacitors has necessitated a demand for new models capable of capturing their dynamics accurately. Such models are useful for design predictions, online estimation and control. In the literature, several models have already been proposed, with these models being generalised into the two types, equivalent circuit and physics based.

Equivalent circuit (EC) models such as [5] and [6] use a parameterised resistor-capacitor (RC) circuit to represent the electrical behaviour of the supercapacitor. The main advantage of this approach is that the resulting model is simple, making ECs a popular modelling approach. However, representing the complex dynamics of an electrochemical device by a RC circuit can have

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limitations. Firstly, the states of the model have no direct physical meaning, making it difficult to infer any understanding of the device from the model. By treating the supercapacitor as a black box in this manner, developing effective control systems becomes problematic and improving the model becomes more challenging. Secondly, the fact that EC models are based upon a parameterisation of a RC circuit means that they are only applicable to one operating condition and any deviation reduces the applicability of the model.

Physics based models instead use a set of conservation and diffusion equations to describe the dynamics of the system. This approach generally involves using a numerical method to solve a system of partial differential equations (PDEs) coupled with algebraic constraints that describe the diffusion and conservation of ions in the supercapacitor. Such models are more generally applicable than the equivalent circuit approach, making model tuning, control and development more intuitive. However, the model is based on a set of PDEs, whose solution is much more complicated to compute than the ordinary differential equations (ODEs) of the EC approach. Subsequently, physics-based models are both more complex and computationally burdensome, a problem which has hindered their adoption.

Examples of such physics-based supercapacitor models include [7] which compares model numerical solutions, obtained using the code of [8], to experimental data. The multi-physics software COMSOL was used in Ref. [9] for a supercapacitor model with non-binary electrolyte. A single-domain, volume-averaging approach using finite elements was implemented in Refs. [10], whose solution could be extended to higher spatial dimensions. In Ref. [11] a comparison of the performances of finite difference, finite element as well spectral methods for a linearised version of the supercapacitor model of [7] was carried out. The spectral methods were found to perform best in this application, being the most accurate for a given number of elements. In addition to numerical methods, an analytical solution for the supercapacitor PDEs, limited to the constant current and impedance spectroscopy operating conditions, is given in Ref. [12]. A review of available commercial software for modelling supercapacitors can be found in Ref. [13].

In the related field of lithium ion battery modelling, there has already been a substantial amount of work on numerical techniques for solving physics based models. In particular, the use of spectral methods has been demonstrated by various authors [14–16]. In Refs. [14], spectral methods were applied across individual finite elements and in Ref. [15] a pseudo-spectral method with Jacobi polynomial basis functions was used, while [16] used a unified approach involving Chebyshev polynomials, with the same method being used to solve all of the equations. In these papers, spectral methods were found to give a marked reduction in model complexity without loss in accuracy when compared to a benchmark finite difference method as well as the COMSOL finite element solver.

As well as being used to capture the dynamic response of a supercapacitor, another important use of the models is to be incorporated within an observer to increase the accuracy of state estimation. An Extended Kalman Filter was applied to an EC model of a supercapacitor in Refs. [17], improving the energy prediction when compared to the straightforward $E = \frac{1}{2}CV^2$ approach, where E is stored energy, C is capacitance and V is voltage. In the related field of lithium ion batteries there has been extensive study on observer design for power management systems [18]. In Refs. [19], an online implementation of a non-linear moving horizon estimator for a reduced order battery model is presented and then used to solve the optimal control problem of maximising the amount of charge stored in a given amount of time.

In this paper, two non-linear models are investigated that simulate the differential algebraic equations that describe a supercapacitor. The first model has a logarithmic non-linearity due to the Nernst–Plank relation [7] while the second has a coupled quadratic (state) non-linearity that accounts for the linear dependence between electrolyte conductivity and concentration. The accuracy of the spectral element and finite difference numerical discretisation methods applied to these models is also investigated, with a finite element solution from COMSOL containing a large number of elements being used as a reference solution. The focus of the models was to be of low order whilst retaining the physical non-linearity as much as possible, so as to give an improved mathematical description of the supercapacitor. A low-order model has the advantage of being less computationally burdensome, making a real-time implementation possible, and also reduces the number of states needed to be estimated by an observer.

The paper is structured as followed. In Section 2, the governing equations of the supercapacitor models are introduced and the various assumptions and mathematical details are explained. Spectral methods are introduced in Section 3 with a brief summary of their convergence and stability properties. Finally, numerical simulation results of the various models are presented in Section 4.

2. Mathematical description of supercapacitor model

The supercapacitor models considered in this paper are based on the four coupled partial differential algebraic equations given in Ref. [7]. The first of these is the Nernst–Plank equation [20], describing the diffusion and migration of ions in the liquid electrolyte phase.

$$U_j = -D_j\left(\frac{\partial c_j}{\partial x} - \zeta_j \frac{F}{RT} c_j \frac{\partial \Phi_2}{\partial x}\right) \tag{1}$$

with the subscript $j = 1, 2$ referring to the positive and negative ions respectively. This equation can be re-written in terms of the variables c, Φ_1, Φ_2 and i_2 as

$$i_2 = -\kappa \frac{\partial \Phi_2}{\partial x} - \kappa\left(\frac{t_+ - t_-}{f}\right) \frac{\partial \ \ln \ c}{\partial x} \tag{2}$$

using the relations

$$U_j = \frac{i_2}{\zeta_j F} \tag{3a}$$

$$\kappa = \frac{F^2}{RT}\frac{1}{2}D\left(\frac{1}{t_-} + \frac{1}{t_+}\right)c \tag{3b}$$

$$D = \frac{2D_- D_+}{D_+ + D_-} \tag{3c}$$

$$f = \frac{F}{RT} \tag{3d}$$

where the transport parameters, such as κ and D, are adapted to account for the effects of porosity and tortuosity [7]. The second of the four supercapacitor equations is Ohm's Law, restricted to the electrode domains,

$$i_1 = i - i_2 = -\sigma \frac{\partial \Phi_1}{\partial x}. \tag{4}$$

The remaining two equations from Ref. [7] are conservation relations, the first for the charge in the electrodes.