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Circuit synthesis of electrochemical supercapacitor models

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ABSTRACT

This paper considers the synthesis of RC electrical circuits from physics-based supercapacitor models that describe conservation and diffusion relationships. The proposed synthesis procedure uses model discretisation, linearisation, balanced model order reduction and passive network synthesis to form the circuits. Circuits with different topologies are synthesized from physical models. Because the synthesized impedance functions are generated by considering the physics, rather than from experimental fitting which may ignore dynamics, this work provides greater understanding of the physical interpretation of electrical circuits and will enable the development of more generalised circuits.

1. Introduction

Electric double layer (EDL) supercapacitors, otherwise known as supercapacitors or ultracapacitors, are an increasingly popular form of energy storage device, which are characterised by high power densities, long lifespans, low temperature dependencies and low internal resistances [1]. The main energy storage mechanism of EDL supercapacitors does not involve chemical reactions, but instead uses charge separation across the double layer in porous electrodes with high specific surface areas [2]. This results in supercapacitors typically having lower energy densities, but higher power densities than devices such as lithium ion batteries, which utilise chemical energy storage, and increased energy densities compared to dielectric capacitors [3]. Supercapacitors are typically used for high power applications, for example, in delivering the transient loads when connected in a hybrid power system with lithium ion batteries [4]. In a hybrid power system, the benefits of the different devices can be combined to give improved performance and reduced battery degradation, since the battery can then be operated at near steady-state conditions.

The growing popularity of supercapacitors has led to a demand for improved performance and understanding from a systems perspective. An important tool to achieve this improved performance is the development of models that enable predictions to be made about the supercapacitor during a charge, reducing experiment numbers and enabling a constructive methodology for design. The literature on supercapacitor modelling is both large and growing, with the models being mainly differentiated by their accuracy, complexity and detail. The two main categories of supercapacitor models are equivalent circuits (EC) and physics based (PB) models. EC models are formed by the connection of passive circuit components such as resistors and capacitors [5]. For supercapacitors, the resulting model equations are typically low-order linear ordinary differential equations (ODEs) which are relatively straight forward to solve. This makes EC models both simple to implement and to understand, resulting in them being the most popular form of model for application purposes. The main drawback of EC models is that the model states have little physical interpretation and the developed circuits are typically local approximations of the nonlinear devices. This limits their use for design purposes and for gaining a detailed understanding about the physical state of the device during a charge. Numerous EC models have been presented in the literature [6–8], with three common circuits being compared in [9] for an electric vehicle application.

PB models are formed from a set of partial differential equations (PDEs) that describe the electrochemistry of the device. These PDEs typically describe diffusion equations coupled with algebraic constraints to enforce charge conservation [10]. Since the underlying equations are PDEs, PB models are generally more complex than EC models and are usually implemented with

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some form of spatial discretisation technique, such as the finite difference method [10]. In [10], the physical PDE equations were established and shown to match experimental data reasonably well. Several studies have expanded upon this PB model, for example, by studying electrode 3D effects and parameter sensitivities [11], the computational implementation with an efficient spectral collocation discretisation [12], implementation with the multi-physics modelling programme COMSOL [13], a reduced order PDE system where concentration effects were ignored [14], the inclusion of temperature effects [15] and analytic solutions for constant current and electrical impedance spectroscopy charging profiles are given in [16]. Physics based models have also been developed for related electrical energy storage devices. For example, the Newman model [17] has been widely studied for lithium-ion batteries, both in terms of its implementation [18] and its incorporation within a control system [19].

Even though both EC and PB supercapacitor models describe the same physical device, there has not been much overlap between the two methods and they are often treated as two separate approaches. Those efforts that have been made to link the approaches tend to give a qualitative, rather than quantitative, relationship between the two. The purpose of this paper is to bridge this gap by linking the two approaches using a mathematical transformation, such that equivalent circuits can be synthesized from the physical PDEs. This mathematical transformation uses balanced model order reduction [20] and passive network synthesis [21]. In order for circuits to be realised, it is necessary to give a state-space realisation of the impedance function. State-space realisations of analytic impedance functions using model order reduction and Taylor series expansion for PB lithium ion models was studied by Smith et al in [22,23] and this paper is concerned with the circuit synthesis of similar realisations. The work of this paper could be said to generalise [24], where a specific circuit is designed to describe a PB lithium ion model, since the goal of this paper is show that a wide *class* of PB models can be synthesised into a wide *class* of circuits. The circuits developed by this approach have a physical basis and should be more robust than those which fit an impedance function to data.

It is stressed that the presented method does not give analytic expressions for the various components of the synthesized circuits in terms of the physical parameters of the device. Instead, a numerical procedure is introduced that allows the circuit synthesize to be efficiently carried out. The reason no analytic expression can be obtained is due to the model order reduction which results in a loss of model information. It should be noted that this work does not focus on model *development*, but instead on PB model *analysis* in terms of electrical components. For this reason, the models considered in this paper are not validated against experimental data, but, this validation was considered in [10,25] amongst others.

The paper is structured as follows; PB and EC supercapacitor models are respectively described in Sections 2 and 3. Section 4 describes the synthesis process that uses passive network synthesis and model order reduction to form circuits from the PB model.

2. Physics based models

A particular PB supercapacitor model will now be described for the purpose of circuit synthesis but it is noted that the synthesis process of Section 4 is flexible enough to be applied on other PB models described by different physical equations. This PB model was developed in [12] and is a reformulation of the model set out in [10]. For the purposes of this paper, this PB model is treated as a 'true' model which describes the whole dynamics of the device and was shown to match up with experimental data [10,25]. The model has three domains, one for each electrode and one for the separator, with the electrically insulating separator preventing a short circuit. In order for the model to be tractable, several assumptions have to be introduced, as outlined in [10]. These include the homogenisation of the electrode structure using porous electrode theory and fixing the capacitance as a lumped parameter, even though capacitance has been shown to change with variables such as the voltage [26]. The boundary conditions of the model are also outlined in [10] and are applied at the separator/electrode and current collector/electrode interfaces. These boundary conditions can be summarised as enforcing conservation of ionic flux and current. The current collectors are responsible for the transfer of current to and from the system. This setup is shown in Fig. 1.

The three partial differential algebraic equations of the PB model describe:

- Charge conservation across the double layer

$$aC\frac{\partial(\phi_1-\phi_2)}{\partial t}=\sigma\frac{\partial^2\phi_1}{\partial\chi^2} \tag{1a}$$

- Elctrolyte diffusion

$$\epsilon\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial\chi^2}-\frac{aC}{F}\left(t_-\frac{dq_+}{dq}+t_+\frac{dq_-}{dq}\right)\frac{\partial(\phi_1-\phi_2)}{\partial t}, \tag{1b}$$

- Ohm's law

$$\kappa\left(\frac{RT(t_+-t_-)}{F}\right)\frac{\partial}{\partial\chi}\ln(c)+\sigma\frac{\partial(\phi_1-\phi_2)}{\partial\chi}+\left(\kappa\frac{\partial}{\partial\chi}+\sigma\frac{\partial}{\partial\chi}\right)\phi_2+i=0 \tag{1c}$$

with specific capacitance aC, potential in the electrode ϕ_1, potential in the electrolyte ϕ_2, electrode conductivity σ, porosity ϵ, diffusion constant D, Faraday constant F, transference numbers t_+ and t_-, $dq_{+/-}/dq$ describing the change in surface concentration of an ion associated with a change in the surface charge on the electrode q, electrolyte conductivity κ, gas constant R, temperature T, current density i and spatial co-ordinate χ. The values of these parameters used in this model based on a SAFT America supercapacitor are given in Table 1. The output of the model y is the voltage V

$$y=V=\phi_1|_{x=0}-\phi_1|_{x=L}. \tag{2}$$

In the electrodes, Eqs. (1a)–(1c) have state-space form (3a) and the state space form of the separator is given by (3b).

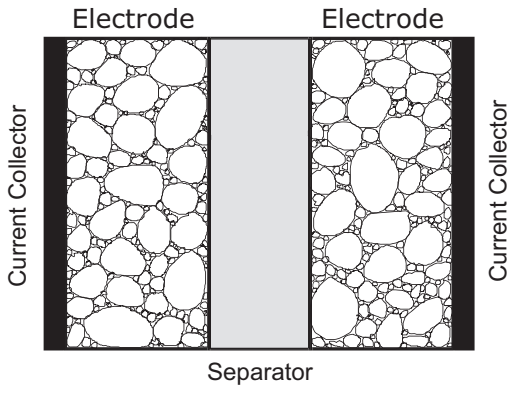

Fig. 1. The standard construction of a supercapacitor.