Journal of Power Sources 256 (2014) 369–382

Contents lists available at ScienceDirect

Journal of Power Sources

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

A generalized multi-dimensional mathematical model for charging and discharging processes in a supercapacitor

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HIGHLIGHTS

- Generalized 3D computational model of an electric double layer supercapacitor.
- 3D microstructural aspects do not have a significant impact on the performance.
- Specific capacitance, ionic conductivity, and tortuosity are critical.
- State-of-the-art numerical methods provide accurate and robust solutions.

ARTICLE INFO

Article history:
Received 18 November 2013
Received in revised form
11 January 2014
Accepted 13 January 2014
Available online 23 January 2014

Keywords:
Supercapacitors
Computer modeling
Electrochemical modeling
Multidimensional simulations
Energy storage

ABSTRACT

A generalized three dimensional computational model based on unified formulation of electrode–electrolyte system of an electric double layer supercapacitor has been developed. This model accounts for charge transport across the electrode-electrolyte system. It is based on volume averaging, a widely used technique in multiphase flow modeling ([1,2]) and is analogous to porous media theory employed for electrochemical systems [3–5]. A single-domain approach is considered in the formulation where there is no need to model the interfacial boundary conditions explicitly as done in prior literature ([6]). Spatio-temporal variations, anisotropic physical properties, and upscaled parameters from lower length-scale simulations and experiments can be easily introduced in the formulation. Model complexities like irregular geometric configuration, porous electrodes, charge transport and related performance characteristics of the supercapacitor can be effectively captured in higher dimensions. This generalized model also provides insight into the applicability of 1D models ([6]) and where multidimensional effects need to be considered. A sensitivity analysis is presented to ascertain the dependence of the charge and discharge processes on key model parameters. Finally, application of the formulation to non-planar supercapacitors is presented.

1. Introduction

Ultracapacitors or supercapacitors are charge storage devices that operate on the principle of electrochemical double layer (ECDL) capacitance wherein, electrical energy can be stored and released by nanoscale charge separation at the interface between the electrode and the electrolyte. In paper [7] advances in electrode materials for the supercapacitor are summarized. There has been considerable activity in the recent years to exploit high surface area offered by Nanotubes [8–14] and more recently Graphene [15]. Most of the projected gains in energy densities (getting closer to that of current Li-ion batteries) are due to increase in capacitance through increase in surface area and exploiting the nano-pore and ion interactions. However, considerable development needs to be done at the system level to ascertain the true performance in a practical supercapacitor [16]. In this work, we developed a macroscopic model that can rapidly use the microscale properties to assess the overall performance of the supercapacitor device and possibly aid in transition of this rapid progress in supercapacitor electrode materials into high performance supercapacitors without lot of iterations at the device level where one needs to balance the cathode, anode, electrolyte, and current collectors to maximize energy and power density.

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http://dx.doi.org/10.1016/j.jpowsour.2014.01.054

Advantages in using the nanoporous carbon materials with fine tuned pore sizes for the corresponding electrolytes is well established. Especially, the cathode and anode with different pore sizes that match the anion and cation sizes could lead to improved power delivery. Aspects such as high conductivity and surface area of these carbon material characteristics are studied for various engineered carbon material with tailored pore-size distribution for high capacitance [10,11,17].

The amount of energy stored in a supercapacitor is inversely proportional to the thickness of the double layer and directly proportional to the specific surface area of the electrodes. By using nanoporous electrodes, supercapacitors deliver a sufficiently high power density compared to conventional batteries and an extremely high energy density compared to conventional dielectric capacitors. However, the energy density of supercapacitor devices are an order of magnitude lower than current battery devices.

They are also amenable to a variety of applications ranging from energy-smoothing, regenerative braking to power-source in hybrid vehicles. Supercapacitors have the advantage of long operating life, a wide thermal operating range, low weight, low maintenance and near infinite cyclability (charge–discharge).

A Ragone plot (see Fig. 1) shows the power density vs. energy density for common energy storage/conversion devices.

Currently, ultracapacitors need coupling with batteries to supply energy for a prolonged time period [18]. One of the motivations for developing novel materials is to increase their energy density and better simulation models can accelerate the adoption of the most promising materials from a full system perspective. In addition, several new designs at the system level can be explored to maximize the energy density while retaining very high power density and life. This requires a careful understanding of the physics at the nanoscale as well as the device scale. While there is a significant increase in research at the nanoscale [11,12,19,20], there is much work to be done at the device scale. Even recent publications e.g. Ref. [6] still consider the electrode properties to be isotropic and the simulations are done in one-dimension. With the advent of new graphene based electrode materials that are utilized for the ultracapacitor [21], due to its high surface area such as 2630 $m^2 g^{-1}$ [22], the accuracy of these assumptions with reference to truly nanostructured materials like chemically modified graphene and carbon nanotube solids have not been addressed. Also, most of these models assume the capacitance in the electrode pores (due to ECDL) can be modeled using parallel-plate assumption. It has been shown recently that capacitance exhibits a strong dependence with pore size and curvature [11,20]. Lanzi and Landou [23] show macroporous structure is important in determining the ohmic and mass-transfer resistance whereas in micropores these effects are negligible because transport is too localized. They also find that distribution in pore volume between macropores and micropores can have a major effect on porous electrode performance. Increase in porous material surface area for different activated carbon material and its influence to the capacitor performance i.e., specific capacitance, one of the important characteristics of the carbon electrode material, has been established [24,25].

In this paper, we test the validity of the first assumption, namely, the effect of anisotropy in electrode properties on the capacitance, charge and discharge characteristic of a ultracapacitor.

For our model, we consider an ultracapacitor unit-cell as shown in Fig. 2 comprising of two nanoporous electrodes isolated from electrical contact through a porous separator. The pores are filled with an electrolyte that allows ionic current to flow through the electrodes while preventing self-discharge. Current collectors typically made of metal foils drain the electrical current from each electrode. In a full-scale system, multitude of these unit-cells are used. For our modeling purpose, it is sufficient to characterize one of these unit-cells.

A historical perspective on modeling electrode-electrolyte interface as circuit has been presented by Geddes [26]. The macroscopic models are primarily based on electrical circuit models or simple 1D/pseudo-2D models [27,28]. V. Srinivasan and J. W. Weidner [29] developed analytical models for the capacitors under constant current while neglecting the electrode kinetics. Pillay and Newman [30] have studied the influence of side reactions using Tafel kinetics on performance of EDCL. A mathematical model is proposed by Ong and Newman [31] for double layer capacitor and the predictions show slower charge build-up due to double layer

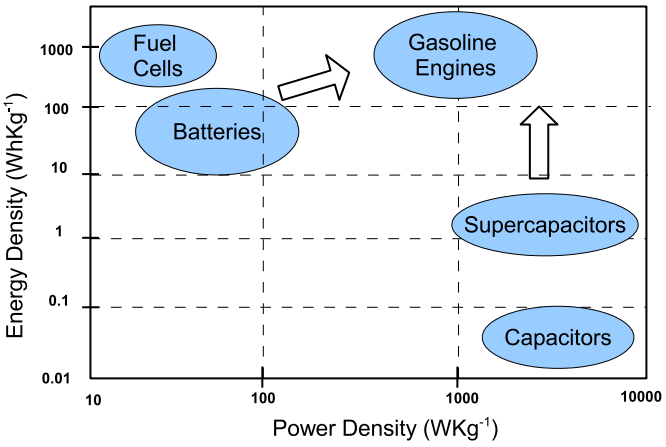

Fig. 1. A Ragone chart showing the power vs. energy densities for a number of energy storage devices and compares that to a gasoline engine. It can be noticed that ultracapacitors have almost 1000 times the energy density of dielectric capacitors and around 10 times the power density of conventional batteries. Units in this figure have been modified to be consistent with the journal requirement.

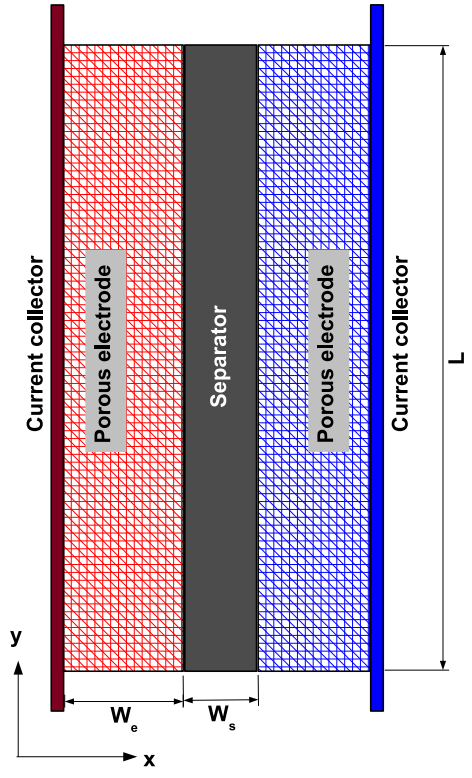

Fig. 2. Schematic of an electrochemical double-layer supercapacitor. The electrodes are typically made of a nanoporous material. The porous separator and the electrode pores are saturated with the electrolyte.