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Reduced-order physics-based modeling and experimental parameter identification for non-Faradaic electrical double-layer capacitors

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ABSTRACT

Electrical double-layer capacitors (EDLCs, also known as supercapacitors or ultracapacitors) are energy storage devices that possess very long cycle life and high power density, but typically have lower energy density than lithium-ion cells. Applications that require both high energy and power density may use hybrid energy-storage systems built using a combination of EDLC and lithium-ion cells. Optimal controls for such systems must be physics-based to optimize the performance they deliver while maximizing life, as performance and degradation are determined by electrochemical variables internal to the devices and not by externally measurable values. Further, for practical application, the models used in the controls must be simple and share a common framework. Accordingly, in this paper we develop a reduced-order physics-based model of a non-Faradaic EDLC that has the same form as a model previously reported for a lithium-ion cell. We show how to determine model parameter values from simple laboratory tests using standard lab equipment, not requiring device teardown to do so. We validate the model against data collected from a commercial EDLC.

1. Introduction

Present-day plug-in hybrid and electric vehicles rely almost exclusively on advanced lithium-ion cells for energy storage, but despite new materials, evolving designs, and improved performance, these cells still possess limitations. One is their relative inability to handle high charge/discharge rates from hard acceleration and/or regenerative braking events without sustaining physical damage that causes permanent performance degradation. Methods or devices that can be used to mitigate the adverse effects of high current are worth investigating.

In contrast to lithium-ion cells, electrical double-layer capacitors (EDLCs, also known as supercapacitors or ultracapacitors) can sustain very large currents and commonly have lifetimes of well over 100,000 charge/discharge cycles with little degradation, while lithium-ion batteries begin to show aging after only a few thousand charge cycles [1]. On the other hand, EDLCs have lower energy density and operating voltage. Marrying energy-dense lithium-ion cells with power-dense EDLCs could bring the best of both to a single energy-storage system (ESS).

ESS engineers have been combining these two types of systems for several years [2–5]. However, there remains room for improvement in controls for such hybrid systems: to do so optimally, we would like to have physics-based models of both lithium-ion cells and EDLCs, since performance limits are determined most directly from internal electrochemical variables such as internal potentials and charge-carrier concentrations and not by external signals such as voltage. Further, we would like models of these two types of device to be computationally simple and to share a common mathematical framework to fit into a comprehensive hybrid controls optimization strategy.

Here, we apply a previously reported method that creates physics-based reduced-order models (ROMs) of lithium-ion battery cells [6–9] to the problem of modeling EDLCs. The methodology begins with continuum-scale partial-differential equations (PDEs) of the dynamics of the electrochemical variables of interest. Laplace-domain transfer functions are derived from these equations. The discrete-time realization algorithm (DRA) automatically reduces these complicated transcendental transfer functions into an optimal reduced-order discrete-time state-space model form. Very low-order models having a total of five states (i.e., uncoupled discrete-time difference equations) can predict all EDLC electrochemical variables at any spatial location in the EDLC as well as device voltage with very high accuracy. Using this approach for EDLC results in a reduced-order physics-based model that has the same discrete-time state-space model structure as previously reported for the lithium-ion cell, so both could fit well together in a hybrid ESS controls optimization strategy.

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Nomenclature

a_s	volumetric specific surface area of electrode, $m^2\ m^{-3}$
A	current-collector plate area of the electrode, m^2
A_s	total interfacial surface area of capacitor, which is different from A in a porous electrode, m^2
$\mathbf{A}$	state transition matrix of the state-space model
$\mathbf{B}$	input matrix of the state-space model
C	double-layer specific capacitance, $F\ m^{-2}$
C_{tot}	electrode's total capacitance, F
C_{dev}	device's total capacitance, F
$\mathbf{C}$	output matrix of the state-space model
$\mathbf{D}$	feedthrough matrix of the state-space model
i_{app}	applied EDLC current, A
i_{dl}	double-layer current density $A\ m^{-2}$
L	length of an EDLC region, m
R_0	series resistance of the EDLC, Ω
R^s	separator resistance, Ω
R_{ss}	steady-state resistance to a steplike input, Ω
t	time, s
$v(t)$	EDLC voltage, V
$\mathbf{x}_k$	state vector of state-space model at time index k
$\mathbf{y}_k$	vector of EDLC electrochemical variables and/or device voltage at time index k

Greek variables

ε	volume fraction of phase indicated by subscript, unitless
ϕ	potential of the phase indicated by subscript, V
κ_{eff}	effective electrolyte conductivity, $S\ m^{-2}$
$\nu(s)$	normalized impedance ratio, unitless
σ_{eff}	effective solid conductivity, $S\ m^{-2}$

Subscripts

e	pertaining to the electrolyte phase
k	discrete-time sample index
s	pertaining to the solid phase

Superscripts

n	pertaining to the negative electrode
p	pertaining to the positive electrode
s	pertaining to the separator region

The remainder of this paper is organized as follows. First, we review the principles of EDLC operation. Second, we reformulate a physics-based continuum-scale PDE model of an EDLC from the literature to be compatible with our approach, derive transfer functions from the PDE model, review the DRA, and use simulation to show that the reduced-order model predictions match the full-order PDE model predictions very well. Third, we show how to extract a particular EDLC's physics-based model parameter values from simple laboratory tests, and demonstrate the method for a commercial EDLC. We close the paper with some discussion and a summary.

2. Principle of EDLC operation

EDLCs, like all capacitors, work on the principle of energy storage via charge separation, which is accomplished by the application of a potential difference between two conductive materials with a non-conductive dielectric region between them.[1] Electrostatic forces cause the two oppositely charged sides to try to equalize by recombining, and when an external conductive path is established between the two sides, the charges recombine and do work in the process.

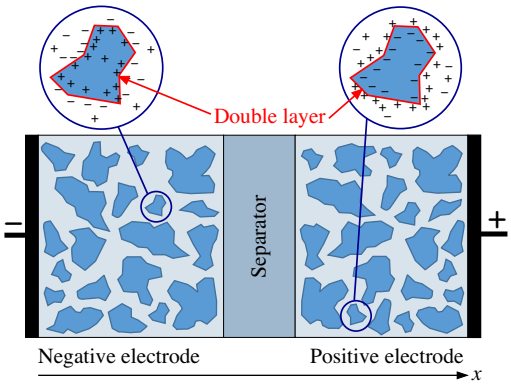

Fig. 1. EDLC internal structure.

The amount of charge that can be stored by a device, per unit voltage, is known as its capacitance. This quantity C_{dev} is measured in Farads and is modeled as

$$C_{dev} = \frac{Q}{V} = \frac{\varepsilon A_s}{d}, \tag{1}$$

where Q is the amount of stored charge in coulombs, V is the potential difference in volts across the dielectric, ε is the permittivity of the dielectric separating the charges, A_s is the total surface area of each electrode, and d is the thickness of the dielectric.

To achieve capacitance, EDLCs consist of three major parts as illustrated in Fig. 1: two identical porous electrodes, a thin porous paper or membrane separator, and an electrolyte permeating the pores throughout the entire device.

2.1. Electrodes

The (usually identical) electrodes are typically manufactured from electronically conductive microscopic particles of activated carbon that are chemically bonded to a metal foil or mesh current collector [12]. The total surface area A_s of all the particles in an electrode is enormous due to this porous-electrode structure.

When potential is applied between the two electrodes, electrons quickly work their way into or out of the solid part of the electrode, causing the surface of the particles to become negatively or positively charged, respectively. Ions present in the electrolyte accumulate near opposite charges on the surface of the solid, forming a surface layer. A second layer of ions—opposite in charge to the surface layer—builds up in the electrolyte adjacent to this surface layer. These two layers of charge in the electrolyte form what is known as the double layer, and it is this double layer that

[1] We distinguish between EDLCs—which operate using the non-Faradaic charge-separation principle—and pseudo-capacitors. Unlike EDLCs, pseudo-capacitors do not have identical electrodes but instead use activated carbon for one electrode while using a more battery-like material such as ruthenium-oxide for the other. Thus, they operate both electrostatically, as do EDLCs, and Faradaically, as do lithium-ion cells. Lin [10] and Popov [11] independently developed physics-based models describing the ruthenium-oxide pseudo-capacitor behavior, and it is possible to extend the models in this paper to include Faradaic processes [9]. However, pseudo-capacitors are more complex to manufacture and are thus more expensive than EDLCs, and they also do not have the expected cycle lifetime as EDLCs. The study of pseudo-capacitors is not within the focus area of this paper.