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Electrochemical double layer capacitor electro-thermal modelling

Wasim Sarwar[a], Monica Marinescu[a], Nick Green[b], Nigel Taylor[b], Gregory Offer[a,*]

[a] Department of Mechanical Engineering, Imperial College London, Exhibition Road, London SW7 2BP, UK
[b] Hybrids and Electrification Research, Jaguar Land Rover, University Road, Coventry CV4 7AL, UK

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ABSTRACT

An electro-thermal model is generated to predict the internal temperature of an electrochemical double-layer capacitor (EDLC) undergoing high current charging/discharging. The model is capable of predicting the electrical and thermal behavior of a cell over a wide range of operating conditions. Spiral symmetry is used to reduce the heat generation and transfer model from 3D to a pseudo-3D, which runs faster without losing fidelity. Unlike existing models, each element in the developed model retains physical meaning and the electrical model is coupled with a high-fidelity thermal model including material geometries, thermal properties and air gaps. Unequal entropy is calculated using first principles, included in the model and compared to experimental data, and shown to be valid. More entropic heat is generated at the positive electrode than the negative in a typical EDLC, and there is little spatial variation of heat generation rate within the jelly-roll. The heat-transfer model predicts temperature variations within a cell; this study examines these variations for multiple conditions. Whilst undergoing high current charging (2 s, 400 A, 650 F cell), a temperature gradient in excess of 3.5 °C can be generated between the positive terminal and the jelly-roll. The time dependent spatial temperature distribution within a cell is explored.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also commonly referred to as supercapacitors, or ultracapacitors, are energy storage devices which store energy via a physical process of charge separation at the solid/liquid interface. They possess high power density, efficiency and cycle life, but low energy density when compared with batteries.

Given their characteristics, EDLCs are ideally suited to applications requiring high power and highly transient loads such as those seen on hybridized passenger and commercial vehicles. Multiple investigations [1–8], have shown that the addition of EDLCs to batteries in hybridised vehicles reduces the power demanded of the batteries and consequently reduce their temperature rise. This in turn could reduce battery degradation and improve the efficiency of the hybridised energy storage system [5].

When combining batteries and EDLCs, a large portion of the power demand is met by the EDLCs, therefore they will rise in temperature during operation. Repetitive high current charge and discharge pulses, as are common in the automotive environment, can lead to the formation of temperature gradients where the internal structure of the cell is hotter than the surface of the cell. The performance of EDLCs varies with temperature, particularly at low temperatures [9]. Consequently, accurate electric modelling of EDLC performance for high currents over extended time periods requires knowledge of the temperature across the active material.

Furthermore, numerous authors [10–14], have demonstrated that EDLC degradation is highly dependent upon temperature. Faradaic reactions, which are the primary cause of capacitance fade and resistance rise, increase exponentially with temperature, and hence an increase in temperature by 20 °C typically increases degradation by an order of magnitude [14,15].

To determine the temperature variation of a supercapacitor during operation, multiple authors have developed thermal models, which are suitable for a range of applications. For consideration of early cell design, d'Entremont et al. [16] have calculated the reversible and irreversible heat generation during electrical operation using a continuum physical electrical model based on the Gouy–Chapman–Stern approximation of double layer. The model therefore defines the non-uniformity of heat generation throughout the active material. However, the study assumes the use of solid carbon planar electrodes rather than highly porous electrodes.

The majority of works are concerned with the study of commercial EDLCs, where the heat diffusion equation is solved

* Corresponding author.
E-mail address: gregory.offer@imperial.ac.uk (G. Offer).

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Nomenclature

α	$°C^{-1}$ Temperature coefficient of terminal material
A, B, D, F	Dimensionless experimentally derived constants from EIS
C	F Capacitance
C_0	F Primary capacitance
$C_{\mathrm{Branch}\ x}$	F Capacitance of branch 'x'
C_{B1},C_{B2}	F Capacitance of RC branch 1, 2
C_{measured}	F Measured capacitance
C_R	F Re-distribution capacitance
$C_{\mathrm{RC\ Branch}}$	F RC Branch capacitance
$C_{\mathrm{Transmission\_Line}}$	F Transmission line capacitance
C_v	V^{-1} Voltage proportionality of capacitance
e	C Electron charge
I	A Current
k	$m^2\,kgs^{-2}\,K^{-1}$ Boltzmann constant
N	Number of branches
Q	J Heat generated
$R_{\mathrm{Branch}\ x}$	Ω Resistance of branch 'x'
R_{contact}	Ω Contact resistance
R_{ionic}	Ω Ionic resistance
R_{measured}	Ω Measured resistance
R_{Leak}	Ω Leakage resistance
R_{series}	Ω Series resistance
R_{series_0}	Ω Series resistance at initial temperature
T, T_0	°C Temperature, initial temperature
t	s Time
τ	s Time constant
Th_{CC}, Th_{El}, Th_{Sep}	$J\,Kg^{-1}\,°C^{-1}$ Thermal mass of current collector, electrode, separator
S_{dl}	$J\,°C^{-1}$ Entropy of double layer
V	V Voltage
v_0, v_H	m^{-3} Volume occupied by the electrolyte in the uncharged state, and charged state (Helmholtz layer thickness)
x	RC Branch number

Subscript units

+	In relation to the positive ion
−	In relation the negative ion
CC_{Thick}	Current collector thickness
El_{Axial}	Electrode in the y-direction
El_{Spiral}	Electrode in the x-direction
El_{Thick}	Electrode thickness
i	Denotes the turn number within the spiral of the jelly-roll
j	Denotes the discretisation unit number in the y-direction
n	Denotes the number of turns of the spiral of the jelly-roll
m	Denotes the number of discretisation units in the y-direction
Sep_{Thick}	Separator thickness
x	Denotes RC branch number

in one [17], two [18], or three dimensions [19,20]. If solving the heat diffusion equation in one direction, heat transfer occurs through the material thickness of contacting materials, directly between the core of the cell and the outer surface of the can; axial temperature gradients (between the terminals of a Maxwell 650F cell) are not considered. If solving in two dimensions, axial temperature gradients can be considered, however the heat transfer around the spiral of the jelly-roll cannot. If solving in three dimensions, the aforementioned limitations are addressed, at the expense of computational cost. The full 3D model developed by Frivaldsky et al. [20] in Comsol can be used to verify the thermal results of reduced order models, (if the temperature changes are not a result of electrical activity).

The works of Gualous et al. [18] experimentally measure the difference in temperature between the core and the surface of a cell during operation, and latterly model the thermal behavior using a simplified two dimensional heat diffusion equation. These results demonstrate that the core of the cell is hotter than the surface during operation. It must be considered however that the insertion of (non-calibrated) thermocouples into the jelly-roll increases resistance, reduces axial thermal conductivity (some contact welds are missing), reduces radial thermal conductivity (looser winding), and increases the radial temperature gradient between the core and surface of the cell, (via elimination of the air gap between the jelly-roll and can).

The few authors [17,21] who have combined electrical and thermal models to produce electro-thermal models have used lumped thermal models only. The models are capable of providing reasonable estimations of electrical performance and temperature change over a range of electrical and thermal conditions. Berrueta et al. [21] develop a temperature dependant electrical model, but ignore thermal gradients. The works of Parvini et al. [17] do not constrain parameters within logical limits as their electrical model has a capacitance value 10–15 times greater than the capacitance of the cell. The thermal model is lumped with an assumption of a fourth order polynomial cooling rate radially between the core and can, which does not account for the discontinuity of the air gap between the jelly-roll and can.

This paper will focus upon the development of a coupled electro-thermal model capable of predicting temperature variations throughout a cylindrical cell, and subsequently uses this information on thermal gradients to determine the temperature dependent electrical behavior.

2. Modelling

2.1. Overview

The electro-thermal model consists of three distinct yet coupled models; an electrical model, a heat generation model and a heat transfer model. The electrical model, (a physically meaningful equivalent circuit), simulates the flow of charge through the system and determines the voltage response of a cell for a given current input. It defines the currents and resistances used as an input for the heat generation model.

The heat generation model defines the quantity and distribution of the generated thermal energy due to ionic activity and ohmic losses in the electrical conductors. The physical heat transfer model determines the temperature change across the spatially discretised cell, in which different discretisation units are characterised by their geometric and thermal properties. Appropriate boundary conditions are set. The local temperature is an input into the electrical model and it has a direct effects capacitance, internal resistance and contact resistance.

2.2. Heat transfer model

2.2.1. Background

Cylindrical EDLC cells comprise a wound jelly-roll within an aluminium can, where the positive current collectors are welded to one side, and the negative to the other. The jelly-roll consists of sheets of carbon electrodes, aluminium current collectors and