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Non-isothermal electrochemical model for lithium-ion cells with composite cathodes

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HIGHLIGHTS

- Non-isothermal electrochemical model developed for lithium composite cathode cell.
- Experimentally obtained composite cathode property implemented in the model.
- Model validated for a wide range of temperature and discharge rate.
- Results analyzed to determine the heat generation pattern in the cell.

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ABSTRACT

Transition metal oxide cathodes for Li-ion batteries offer high energy density and high voltage. Composites of these materials have shown excellent life expectancy and improved thermal performance. In the present work, a comprehensive non-isothermal electrochemical model for a Lithium ion cell with a composite cathode is developed. The present work builds on lithium concentration-dependent diffusivity and thermal gradient of cathode potential, obtained from experiments. The model validation is performed for a wide range of temperature and discharge rates. Excellent agreement is found for high and room temperature with moderate success at low temperatures, which can be attributed to the low fidelity of material properties at low temperature. Although the cell operation is limited by electronic conductivity of NCA at room temperature, at low temperatures a shift in controlling process is seen, and operation is limited by electrolyte transport. At room temperature, the lithium transport in Cathode appears to be the main source of heat generation with entropic heat as the primary contributor at low discharge rates and ohmic heat at high discharge rates respectively. Improvement in electronic conductivity of the cathode is expected to improve the performance of these composite cathodes and pave way for its wider commercialization.

1. Introduction

Lithium-ion batteries have become ubiquitous in the field of consumer electronics. These high energy density and light-weight batteries have found application in laptops, mobile phones, cameras and other consumer products [1]. With the growing demand for the use of greener alternatives in automotive and aerospace applications, the push for the adaption of lithium-ion batteries as energy source is gaining momentum. The ultimate aim is the large scale electrification of automobiles. Significant challenges still exist to this end and form the focus of intense research. Lithium-ion battery has to exhibit high energy density, high rate capability, thermal stability and long life to meet the standard expected by the automotive industry [2,3].

Oxides of first row transition metals (Mn, Fe, Co, Ni) offer high energy density due to high lithium intercalation site density. The first commercial lithium-ion cell, introduced by Sony in 1991 was a

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Nomenclature

A	fitting coefficients for NCA OCP
a	volumetric area ($m^2\ m^{-3}$)
B	fitting coefficients for NCA entropy generation
C	specific heat/heat capacity ($J\ kg^{-1}\ K^{-1}$)
c	concentration of Li ($mol\ m^{-3}$)
D	diffusivity ($m^2\ s^{-1}$)
E	potential (V)
F	Faraday constant (96485 $Qmol^{-1}$)
$f_{\pm}$	mean molar salt activity coefficient
h	heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
i	current density ($A\ m^{-2}$)
k	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
N	number of data points
R	radius (m)
R_g	universal gas constant (8.3145 $J\ mol^{-1}\ K^{-1}$)
r	radial coordinate (m)
Q	heat source ($W\ m^{-3}$)
T	temperature (K)
t	time (s)
t_+^0	transference number of the electrolyte
V	cell voltage (V)
x	through plane coordinate (m)
y	cathode state of charge

Greek letters

α	transfer coefficient
ε	porosity
κ	ionic conductivity ($S\ m^{-1}$)
ρ	density ($kg\ m^{-3}$)
σ	electronic conductivity ($S\ m^{-1}$)
ϕ	potential (V)

Subscripts

a	anode
c	cathode
e	electrolyte phase
eq	equilibrium
exp	experimental
i	particle interface/surface
irr	irreversible
mod	model
n	intercalation
P	constant pressure
p	particle
rev	reversible
s	solid (electrode) phase
tot	total
ohm	Ohmic heat generation
0	initial condition, exchange

Superscripts

eff	effective
max	maximum
ref	reference

$LiCoO_2$/C cell [4]. Due to high cost of cobalt and low cycle-life however, $LiCoO_2$ is not suitable for large scale applications like electric vehicle. Nickel-based cathode has a similar structure with lower cost and higher energy density as compared cobalt-based cathode [5]. On the other hand, $LiNiO_2$ is more prone to lattice disorder and hence, difficult to adapt for large scale production. The addition of cobalt in the $LiNiO_2$ structure stabilizes the compound, both from lattice disorder and oxygen loss perspective [6]. High temperature instability of nickel-based cathodes has been investigated by various researchers [7–10]. The reason for thermal instability is attributed to oxidation of organic solvent by the oxygen produced due to degradation of lithium nickelate [10]. Doping the lithium nickel cobalt oxide with aluminum or magnesium improves the thermal behavior and cyclic capacity [11]. The initial

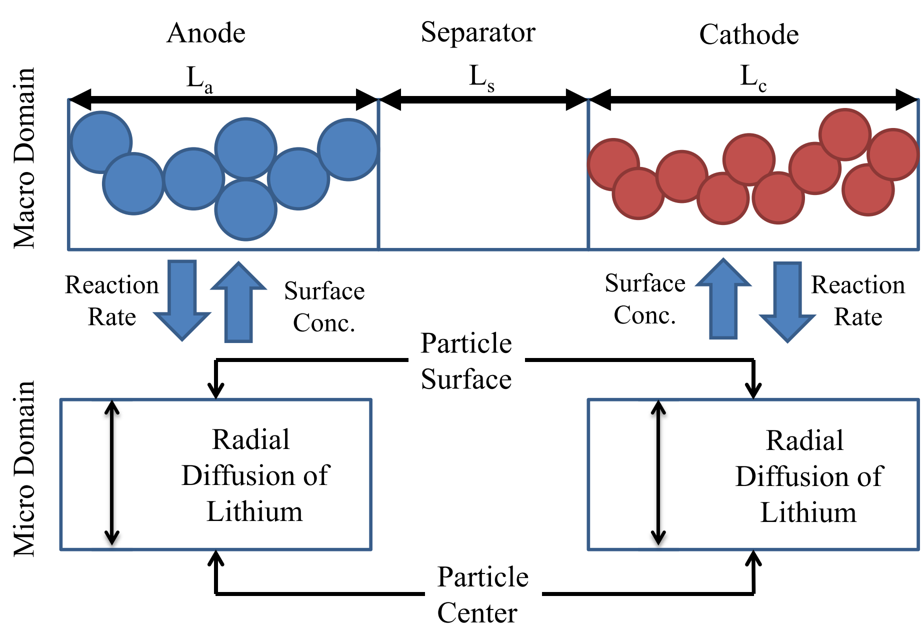

Fig. 1. Schematic of LiNCA computational model.