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# Quantification of bottlenecks to fast charging of lithium-ion-insertion cells for electric vehicles

Rajeswari Chandrasekaran

*Research and Advanced Engineering, Ford Motor Company, Dearborn, MI 48124, USA*

## HIGHLIGHTS

- Validated the lithium-ion cell sandwich model with experimental charge data.
- Quantified and analyzed the overpotential contributions at high charge rates.
- Magnitude of overpotentials increase with charge rate.
- Thermodynamic conditions favorable for lithium plating exist in the negative electrode from 2C charge rate.

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## ABSTRACT

In this work, an isothermal, physics-based, dual lithium-ion insertion cell sandwich model is used for simulating the galvanostatic charge performance of a graphite ($Li_xC_6$)/liquid electrolyte/$Li_y(Ni_aCo_bMn_c)O_2$ at room temperature at various current densities. The modeling results are compared with experimental cell potential vs. capacity data. The validated model is used to identify the bottlenecks to fast charging by quantification of the various contributions to the cell overpotential. Lithium plating at the negative electrode is shown to be thermodynamically feasible during galvanostatic charging at 2C rate and above. This work will aid in research and development activities to overcome the hurdles to fast charging of advance electric vehicle batteries.

## 1. Introduction

Vehicles with different levels of electrification are in the portfolio of most major automobile manufacturers to reduce tail pipe emissions, deliver higher fuel economy, and increase energy security by reducing dependence on foreign oil while delivering vehicles with good performance, durability, customer satisfaction and acceptable range [1]. Presently, the recharge time for battery electric vehicle (BEV) and plug-in hybrid electric vehicle (PHEV) is long compared to the refuel time for gasoline powered vehicles. For electric vehicles, the ability of a system to charge at high rates could be just as important as high-rate discharges [2] as it leads to increased customer acceptability by reducing range anxiety. Better fast charge acceptance also means improved ability to capture regenerative braking energy in hybrid electric vehicles. Charging at $\geq$ 2C rate or at even extreme rates of 10–20C rate should in principle deliver a fully charged pack in 30 min and 6–3 min respectively. The US Department of Energy (DOE) has set a fast charge goal [3] of 10 miles of range per minute of fast charge. For an EV with 100 mile range (24 kWh battery pack), the DOE goal is to enable a full charge in 10 min (6C rate) and for a PHEV with 40 mile electric range (12 kWh battery pack) in 4 min (15C rate). If fast charging is such an important attribute, the question arises as to why fast charging is not widely available.

Researchers have been studying various methods to fast charge lithium-ion batteries, their effects on performance and capacity fade [4,5]. During charging, when a constant-voltage step is employed after a constant-current step, the total charging time initially decreases with increasing current [5]. It is not obvious how the total charging time will change with faster charge rates because of the various coupled phenomena occurring in the cell.

In one attempt to deliver a cell capable of fast potentiostatic charging, novel electrode architecture was reported in literature [6]. However, the capacity of the graphite negative electrode was

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*E-mail address:* rchand35@ford.com.

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designed to be ten times more than that of the positive electrode. This is not a practical ratio for lithium-ion cells for electric vehicles. Advances in positive electrode materials such as $LiFePO_4$ have been discussed in detail about their ability to sustain fast charging rates [7–9]. However, the weight percent of the conductive carbon was varied from 15% to 65% depending on the intended charge rate [7,9] and likewise impractical for automotive batteries. Several bottlenecks can limit the charge acceptance of an electric vehicle battery pack at high rates. Limitations to charging the coke/plasticized electrolyte/spinel sandwich up to 1.3C rate is available in literature [2]. In an earlier work, [1] the overpotentials arising from various mechanisms were systematically quantified and analyzed to identify the bottlenecks or limitations during fast charging (at 3C and 10C rate) of the coke/liquid electrolyte/spinel lithium-ion cell sandwich [10] from simulations. However, presently most lithium-ion cells employ a graphite based negative electrode with a positive insertion electrode and the electrodes are relatively thinner (and sometimes less porous) than before [11]. Therefore, it is worthwhile to analyze the bottlenecks to fast charging in these systems which are more representative of the current state of the art to better understand the origin of their limitations and possible approaches to improvement.

Quantification of contributions to cell overpotential during galvanostatic discharge of a graphite($Li_xC_6$)/liquid electrolyte/$Li_y(Ni_aCo_bMn_c)O_2$ cell sandwich were carried out recently [12] using an experimentally [11] validated physics-based model. However, it is imperative to analyze the bottlenecks to fast charge acceptance separately because: (a) the upper cut-off potential is closer to the thermodynamic open-circuit potential of the cell than the lower cut-off potential and therefore the rate capability effects may be more pronounced during charge than discharge of a dual lithium-ion insertion cell, contributing to the asymmetry in the obtained capacities [2], and (b) limitations to fast charging (and the asymmetry between charge and discharge capacity especially at high rates) can be due to the low thermodynamic open-circuit potential of the carbon based negative electrodes (such as graphite [13] or coke [10] in some cases) at high lithium content as this can lead to lithium plating under significant overpotential.

Therefore, the isothermal physics-based model [12] of the graphite ($Li_xC_6$)/liquid electrolyte/$Li_y(Ni_aCo_bMn_c)O_2$ cell sandwich was validated with experimental cell potential vs. capacity data during galvanostatic charging at various current densities or rates [14] at room temperature. In the present work the contributions to cell overpotential during galvanostatic fast charge of these advanced lithium-ion cells are quantified and analyzed from simulations with the validated model. Furthermore, thermodynamic insight into the possibility of lithium plating on the negative electrode is also provided. Modeling is an important tool for this research because experimentally measuring the various spatial temporal contributions to cell overpotential that limit the charging process is often difficult or impossible. The knowledge gained from this work will help in research and development activities to overcome fast charging issues in advance electric vehicles.

## 2. Modeling

The galvanostatic charge of $Li_xC_6$/liquid electrolyte/$Li_y(Ni_aCo_bMn_c)O_2$, i.e. dual lithium-ion insertion cell sandwich is modeled using macro-homogenous approach and concentrated solution theory. The underlying theories and equations have been discussed extensively in the past for similar systems [10], [15] and are therefore not repeated here. Although the liquid electrolyte in the experiments is $LiPF_6$ in EC:EMC:DMC in the ratio 3:4:3 with additives [11], for modeling purposes, the liquid phase is considered to be made up of binary electrolyte and a solvent. The thermodynamic open-circuit potential vs. composition curves for the individual electrodes, ionic conductivity of the electrolyte as a function of salt concentration and the experimental charge curves are taken from prior work [11,14]. The experimental galvanostatic charge curves (cell capacity vs. voltage plots) [14] were obtained at 25 °C using an 18650 surrogate cell format with a designed capacity of 230 mAh (21.30 A m$^{-2}$ is the ideal 1C-rate) [11]. In the experiments [14], the cells were galvanostatically discharged at 0.5C rate and a rest period of one hour between the discharge and charge steps was provided. Although cell overpotential of 50 mV is associated with 0.5C rate discharge [12], the relaxation step should help avoid any confounding effects on the subsequent charge step.

Other parameters [11,12,14] are provided in Table 1. The sign of the applied current is negative for charging direction by convention in the simulations. The initial solid lithium concentrations of the individual electrodes for charge are, as expected, different from that for the discharge. The kinetic rate constants have to be slightly decreased at higher charge rates (2C and 3C rates) as seen in Table 1 for a better fit with the experimental curves [14]. The uncertainty in solid lithium concentration at the beginning of charge due to the difficulty in measuring them accurately justifies adjusting this parameter slightly as shown in Table 1 [14] for the positive electrode for a better fit at 3C charge rate.

The simulations of the coupled, transient, partial differential equations at all galvanostatic charge rates are carried out at 298 K, to the cell cut-off potential of 4.2 V (as in experiments) using COMSOL multiphysics finite element software (version 4.3). The

**Table 1**
Model input parameters.

| Parameter description | | Value |
|---|---|---|
| Constant-current density at 1C charge rate | | −21.3 A m$^{-2}$ |
| Radius of the secondary particle of the negative electrode active material | | 6.35 μm |
| C-rates at which the cell is charged | | 0.5; 1; 2; 3 |
| Radius of the secondary particle of the positive electrode active material | | 5.15 μm |
| Transference number | | 0.363 |
| Salt diffusion coefficient | | $7 \times 10^{-11}$ m$^2$ s$^{-1}$ |
| Active material volume fraction in the positive electrode | | 0.62 |
| Electrolyte volume fraction in the positive electrode | | 0.29 |
| Bulk solid matrix electronic conductivity (positive) | | 0.5121 S m$^{-1}$ |
| Bulk solid matrix electronic conductivity (negative) | | 4.3317 S m$^{-1}$ |
| Initial electrolyte concentration | | 1300 mol m$^{-3}$ |
| Active material volume fraction in the negative | | 0.65 |
| Electrolyte (pore) volume fraction in the negative | | 0.33 |
| Maximum solid phase lithium concentration (negative) | | 30,813 mol m$^{-3}$ |
| Maximum solid phase lithium concentration (positive) | | 51,000 mol m$^{-3}$ |
| Initial solid phase lithium concentration (negative) | | 1462.1 mol m$^{-3}$ |
| Initial solid phase lithium concentration (positive) | 0.5C–2C rate | 35700 mol m$^{-3}$ |
| | 3C rate | 36,720 mol m$^{-3}$ |
| Kinetic rate constant (negative) | 0.5C and 1C rate | $1 \times 10^{-11}$ m s$^{-1}$ |
| | 2C rate | $0.6 \times 10^{-11}$ m s$^{-1}$ |
| | 3C rate | $0.4 \times 10^{-11}$ m s$^{-1}$ |
| Kinetic rate constant (positive) | 0.5C and 1C rate | $1 \times 10^{-11}$ m s$^{-1}$ |
| | 2C rate | $0.6 \times 10^{-11}$ m s$^{-1}$ |
| | 3C rate | $0.4 \times 10^{-11}$ m s$^{-1}$ |
| Anodic and cathodic transfer coefficients in the positive and negative electrodes | | 0.5 |
| Geometric cross-sectional area of the cell | | 0.0108 m$^2$ |
| Thickness of graphite (negative porous insertion electrode) | | 59.1 μm |
| Solid phase lithium diffusivity in negative particle | | $2 \times 10^{-14}$ m$^2$ s$^{-1}$ |
| Solid phase lithium diffusivity in positive particle | | $7.49 \times 10^{-13}$ m$^2$ s$^{-1}$ |
| Thickness of the separator | | 21 μm |
| Thickness of $Li_y(Ni_aCo_bMn_c)O_2$ (positive porous insertion electrode) | | 50 μm |
| Separator porosity | | 0.48 |
| Bruggeman exponent in separator | | 3 |