



Internal resistance mapping preparation to optimize electrode thickness and density using symmetric cell for high-performance lithium-ion batteries and capacitors

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HIGHLIGHTS

- An internal resistance prediction map was proposed for LIB electrode optimization.
- New cell design—the counter-electrode-removable symmetric cell—was also proposed.
- Internal resistances were analyzed applying EIS on newly-designed symmetric cells.
- Empirical formula between R_{ct} and electrode density was deduced from EIS analysis.

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ABSTRACT

Methods for characterizing and optimizing the internal resistance of electrodes are crucial for achieving the simultaneous goals of high energy density and high power density in lithium-ion batteries. In this study we propose—and confirm the efficacy of—a method for electrode design optimization based on the construction of an *internal resistance map*, a visualization tool for minimizing electrode resistance. The construction of the map proceeds by identifying the three primary components of the electrode resistance—charge-transfer resistance, ionic resistance, and contact resistance—and elucidating the dependence of each component on electrode density and thickness. We fabricate electrode sheets of various densities and thicknesses and conduct electrode impedance spectroscopy (EIS) measurements to measure the dependence of internal resistance on density and thickness, which we characterize via empirical formulas incorporated into our internal resistance map. Using our map, we predict that the resistance per unit area of a nickel-cobalt-manganese (NCM) electrode attains its minimum value at thickness 70 μm and density 2.9 g cm^{-3} . We then further use the map to predict variations in IR drop for NCM electrodes of different densities, obtaining results in excellent agreement with experimental measurements.

1. Introduction

Efforts to design more sustainable societies have spurred widespread adoption of renewable energy technologies, a trend which is increasingly restructuring fossil-fuel-dependent industrial sectors such as the automobile and heavy-equipment industries [1]. In particular, major nations such as India, France, and England have announced plans to ban the sale of gasoline vehicles within the next few decades,

stimulating efforts to accelerate the transition to more environmentally-friendly options such as electric vehicles (EVs), fuel-cell vehicles (FCVs), and plug-in hybrid vehicles (PHEVs) [2]. However, the lithium-ion secondary batteries that supply the driving energy for electric vehicles continue to exhibit significant unrealized potential compared to gasoline, and the need to improve the performance of these devices—particularly in areas such as energy density, power density, and safety—has become an increasingly urgent challenge. Although it is

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generally understood that a tradeoff exists between energy density and power density, recent years have witnessed active research initiatives targeting simultaneous improvements in both of these quantities, focusing primarily on optimizing the design of cells and electrodes to extract maximum performance from the active materials used to construct electrodes. In particular, the design of electrodes—which ultimately determines the speed and quantity of lithium storage—is one factor that directly impacts the energy and power density of cells, and has thus become a focus of intense effort in both research and development settings [3]. The most common technique for designing high-energy-density electrodes is to increase the quantity of active material per unit area; however, this tends to degrade power density—a consequence generally attributed to increased internal resistance and/or reduced ion diffusivity in composite electrodes as the density or the thickness is increased [4,5]. For this reason, the design of electrodes to achieve desired performance benchmarks is a delicate balancing act requiring a creative combination of strategies. In addition, many applications—including HEVs and batteries for renewable-energy-based electric power generation—require high peak speeds for charge and discharge, further emphasizing the urgent need to elucidate the relationship between electrode structure and electrode internal resistance [6]. However, to date most work on electrode design and internal-resistance optimization has proceeded largely by trial and error, employing simple empirical methods with a heavy reliance on knowhow and guesswork. Moreover, optimal electrode structures differ for each possible choice of electrode material [7]. Clearly, the field is in dire need of common, standardized methods of characterization to improve the efficiency of electrode structure design optimization. In this paper, we take a major step in this direction by proposing a new general-purpose method for understanding the relationship between the structure and internal resistance of electrodes; as an immediate byproduct of our novel approach, we use the new understanding it offers to construct an *internal resistance map* that serves as a powerful tool for rationalizing and accelerating the electrode-design process.

To date there have been several reports of studies investigating the relationship between electrode mass and internal resistance with an emphasis on electrode thickness [8,9]. Ogihara et al. used symmetric cells to characterize the internal resistance of electrodes of varying thickness and fixed electrode density via electrochemical impedance spectroscopy (EIS) measurements; this analysis successfully isolated the primary components of the electrode resistance—namely, the charge-transfer resistance and the ionic resistance in the pores—on the basis of the following equations, derived from the EIS results and a transmission-line model of cylindrical pores [8,10]:

$$Z_{\text{nonfaradic}} = \sqrt{\frac{R_{\text{ion},L}}{2\pi r j\omega C_{\text{dl},A}}} \coth \sqrt{R_{\text{ion},L} j\omega C_{\text{dl},A} 2\pi r L}$$

$$Z_{\text{faradic}} = \sqrt{\frac{R_{\text{ion},L} R_{\text{ct},A}}{2\pi r (1 + j\omega R_{\text{ct},A} C_{\text{dl},A})}} \coth \sqrt{\frac{R_{\text{ion},L} (1 + j\omega R_{\text{ct},A} C_{\text{dl},A}) 2\pi r}{R_{\text{ct},A}}} L$$

Ogihara et al. also demonstrated that the two components of the internal electrode resistance (charge-transfer and ionic resistance) are respectively proportional and inversely proportional to the thickness, i.e.

$$R_{\text{ion}} = R_{\text{ion},L} \times \frac{L}{n} = k_{\text{ion},T} \times L \quad (1)$$

$$R_{\text{ct}} = \frac{R_{\text{ct},A}}{2\pi r L} = k_{\text{ct},T} \times \frac{1}{L} \quad (2)$$

here L and n are the electrode thickness and the number of pores per unit electrode surface area and $k_{\text{ion},T}$, $k_{\text{ct},T}$ are constant coefficients.

On the other hand, the effect of electrode *density* on the relationship between electrode mass and internal resistance has not been adequately characterized to date. Possible reasons for this include (1) previous studies have not attempted to optimize the performance of high-density

electrodes under high-power conditions, (2) it is difficult to fabricate prototype electrodes in research settings (that is, it is difficult to fabricate electrodes of different densities while retaining a constant thickness). Singh et al. fabricated electrodes of various density (porosity) and studied the relationship between electrode density and rate performance; they showed that charge/discharge speeds increase with increasing porosity, while lowering the porosity below a certain threshold value results in a sudden drop in power density [11]. However, studies of this sort have yielded only qualitative conclusions, falling short of providing quantitative insight into the components of the internal resistance. In this study, we fabricate electrodes of various electrode densities at a fixed electrode thickness and use EIS analysis, with data fitted to a transmission-line model [12] [13], to achieve quantitative analysis of internal resistance and isolation of resistance components. In analyzing internal resistance, we use a symmetric cell to eliminate the influence of counter electrodes or reference electrodes [8,10] [14]. Using this cell allows us to avoid contaminating our results with contributions from spurious resistance components, facilitating accurate separation of the resistance of the symmetric electrodes [15]. In previous methods, state of charge (SOC) adjustments for symmetric cells involved a multi-stage process—constructing the full cell, adjusting SOC, deconstructing the full cell, cutting the electrodes, and reconstructing the symmetric cell—which required careful engineering to prevent increases in internal resistance incurred in this process. In this study, we avoid this multi-stage procedure by introducing an original new symmetric-cell design—which we term the *counter-electrode-removable symmetric cell* (CER-SC)—that allows easy insertion and removal of the counter electrode, enabling EIS measurements at varying SOC with no need to deconstruct the cell.

2. Experimental

2.1. Electrode preparation

Positive electrodes were constructed by preparing a slurry consisting of a 91.0/4.5/4.5 mixture of the active material (NCM electrode: $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, Nippon Chemical Industrial Inc.), a conducting agent (acetylene black: DENKA BLACK HS-100, Denka Company Limited), and a binder (PVDF: KF polymer #1120, KUREHA CORPORATION); this was applied as a coating to a current collector (primer coated foil: Nippon Graphite), subjected to preliminary drying at 60 °C for 3 h, then subjected to primary drying at 80 °C for at least 12 h. To fabricate electrodes of fixed thickness and varying density, we used a Baker film applicator (TESTER SANGYO CO., LTD) to construct electrodes of varying masses. To control the electrode density, we performed pressing in a roll press to yield electrodes of constant thickness (50 μm) and various masses.

2.2. Symmetric cell assembly and electrochemical characterizations

All electrochemical characterizations were carried out using coin cells or laminate cells constructed in a dry room (dew point -40 °C). Impedance measurements were carried out using the cell shown in Fig. 1. For electrochemical experiments, we used an electrolyte (1.0 M LiPF_6 EC/DEC, 50/50 vol ratio) and a separator (CELLGUARD2400). The electrodes to be measured were arranged to face each other in a planar configuration and a counter electrode with lithium affixed to both surfaces was inserted between them. To adjust the working electrode SOC, the two working-electrode terminals were shorted together and used as a cathode, while the center lithium electrode was used as an anode; charging and discharging were performed in this half-cell to achieve the desired SOC. Prior to EIS measurements, charge-discharge tests were conducted for NCM electrodes using Li metal counter-electrodes placed in the center of a CER-SC cell, and the potential at 50% SOC was determined based on the slopes of the resulting charge/discharge curves for NCM electrodes. After achieving the desired SOC,

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