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Thermal Simulations of Polymer Electrolyte 3D Li-Microbatteries

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ABSTRACT

High charge and discharge rates are desired properties for Li-ion batteries of both macro- and micro-scale (i.e. a footprint area of $< 1\,mm^2$). Under these conditions, a rise of the cell temperature can take place, leading to performance limitations and safety issues. Investigations of thermal effects in battery cells provide possible explanations of the limiting factors of cell performance and can suggest improvements. We present here extensive simulations with a fully coupled 3D thermal-electrochemical model of 3D microbatteries (3D-MBs) using Finite Element Methodology (FEM). 3D-MB architectures comprising pillar shaped, plate shaped and concentric electrode arrangements are simulated, using $LiCoO_2$ and graphite as electrodes and solid polymer electrolytes with LiTFSI salt. Sensitivity analysis of the electrolyte diffusion coefficient, depending on the C-rate, is used to benchmark the performance of these 3D-MB cells. FEM simulations of the 3D-MB during operation provide a complete 3D time-dependent description of the thermal behavior of the cells. Temperature gradients in the cell highlight critical regions which are likely causing performance bottlenecks and safety hazards. The simulations clearly demonstrate that the highest heat sources appear near the regions with most active charge transfer processes, thereby providing insights for optimization of the cell geometry in terms of both performance and safety.

1. Introduction

Li-ion batteries are rapidly becoming the technology of choice for the next generation of electric vehicles, various consumer electronics and portable devices [1,2]. With their high energy densities, lithium-ion batteries are also targeted for microelectromechanical systems which find applications in broad areas, such as optics and sensors. The need to power these devices is a driving force for developing smaller scale ($\sim 1\,mm^3$) lithium-ion micro-batteries (MB). In these batteries, maximized energy and power density can be achieved by introducing 3-dimensional (3D) electrodes [3–5]. 3D-MBs comprise two electrodes (cathode and anode) in a complex arrangement, e.g., a large number of closely spaced pillars or plates which are separated by polymer or ceramic solid electrolyte [6–8]. Significant achievements have been devoted to develop different material combinations and electrode designs for these 3D-MBs [9–12].

As the need for small-scale portable power sources grows, so do the concerns regarding their longevity, reliability and safety. One single cell may operate very well at room temperature, but in the battery of similar cells, where they all generating heat, it can easily exceed its thermal limits even in properly tested systems [13,14]. Since the performance of the batteries is strongly dependent on temperature, thermal management plays an important role. Moreover, since these systems have complex micro-scale architectures, it remains problematic to prepare full-cell prototypes and it is not yet entirely understood how the design affects the interplay between temperature and the electrochemical processes taking place during charge and discharge cycling [15–18]. Hence, theoretical modeling and computer simulations represent helpful tools for gaining a fundamental understanding in a rapid and cost-effective manner [19–23] and can also provide insights to optimal material usage and battery designs with enhanced performances [24–26].

In this context, battery design can be improved through modeling of the heat transfer in the power source [27]. By utilizing FEM, thermal simulators coupled with detailed models which characterize the electrochemical reactions and transport phenomena taking place inside the battery can be achieved, thereby visualizing internal temperature gradients and identifying hotspots. Previous studies of battery thermal management have focused on the fundamental understanding of battery prototypes

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by numerical simulations. In 2003, Thomas et al. [28] introduced a general energy balance for an electrochemical system, using porous insertion electrodes and assuming uniform temperature. Smith et al. [29] employed a 1D electrochemical model to explore the thermal behavior of a 6-Ah, 72-cell Li-ion hybrid-electric vehicle battery pack, and several other studies [30–33] have covered commercially available cylindrical batteries. Recently, Mao et al. [34] presented a dual foil model to simulate temperature rise in Li-ion cells at very high currents and Kim et al. [35] modelled the thermal behavior of a Li-ion battery during charge. Three-dimensional models of Li-ion battery considering local mass transport and convection dependent effects to reflect the heat dissipation performances are less investigated. However, Samba et al. [36] described the impact of tab location on large format Li-ion cells using a fully coupled 3D modelling, and several studies [37,38] investigate transport phenomena and thermal behavior of electrolytes have been published. In addition, Liang et al. [39] introduced a mathematical model and reliability analysis of a 3D Li-ion battery with a pillar-shaped electrode. These studies have shown that computationally efficient models capable to provide reasonable estimates of the cell thermal distribution with limited calibration efforts and can thus be useful tools for battery pack designers and integrators.

This study describes an approach for analyzing and developing 3D electrode designs and 3D-MB architectures using coupled multiphysics modelling and FEM. The aim of the study is to accurately capture the electrochemical behavior and temperature development in these cells, since these have not been coupled before using FEM for 3D-MBs. Thermal and electrochemical behavior of several 3D-MB architectures at different charging/discharging current rates are compared to each other in order to detect overheated regions and regions of high electrochemical activity caused by inhomogeneous local current densities. Finally, the impact of electrolyte diffusion coefficient (diffusivity) on the temperature and cell performance is also investigated. To meet these objectives, the model has to be both sufficiently simple and accurate enough to provide a reasonable estimation of thermal dynamics inside the electrochemical cell.

2. Experimental

2.1. Simulated materials and battery architectures

In the current study, we use three previously studied [25,26,40,41] MB architectures (Fig. 1): interdigitated (Fig. 1a), concentric (Fig. 1b) and trench (Fig. 1c) geometries. All simulated models comprise cells with porous $LiCoO_2$ (LCO) positive electrodes, porous graphite negative electrodes, and solid polymer electrolyte (1.5 M LiTFSI in poly(ethylene oxide); PEO).

Based on our previous results, we use close to optimal geometrical dimensions for the electrochemical behavior. These comprise of 60 μm long pillars/plates, 20 μm pillar/plate diameter and 5 μm of electrolyte thickness (Fig. 1d) [40]. The MB consists of an array of pillars/plates under periodic boundary conditions. All investigated architectures contain 3D current collectors in the cathodes supporting the pillar/plate structure and increasing the electrical conductivity of the $LiCoO_2$ electrodes.

The initial concentration in the electrolyte is 1500 mol/m^3 and the initial lithiation levels in the LCO and graphite electrodes are 95% and 5%, respectively [20,30]. All systems are initially charged from 3.5 V up to 4.1 V followed by a discharge cycle down to 3.5 V to generate a realistic initial ion distribution in the electrodes and electrolyte. Thereafter, the discharge process is simulated and analyzed. At first, the voltage profile and gravimetric capacity (mAh/g) per gram of cathode material (LCO) of different architectures is studied and compared. Second, applied external current density per cell footprint area is varied between 1 A/m^2, 4 A/m^2 and 10 A/m^2 (roughly corresponding to 0.3, 1.3 and 3.6 C-rate) in the conducted simulations to compare the performance of different 3D-MB architectures. Lastly, these studies are followed by a set of simulations where a liquid electrolyte was used under the constant current density (4 A/m^2) in order to determine the impact of liquid and polymer electrolytes on the cell performance and temperature.

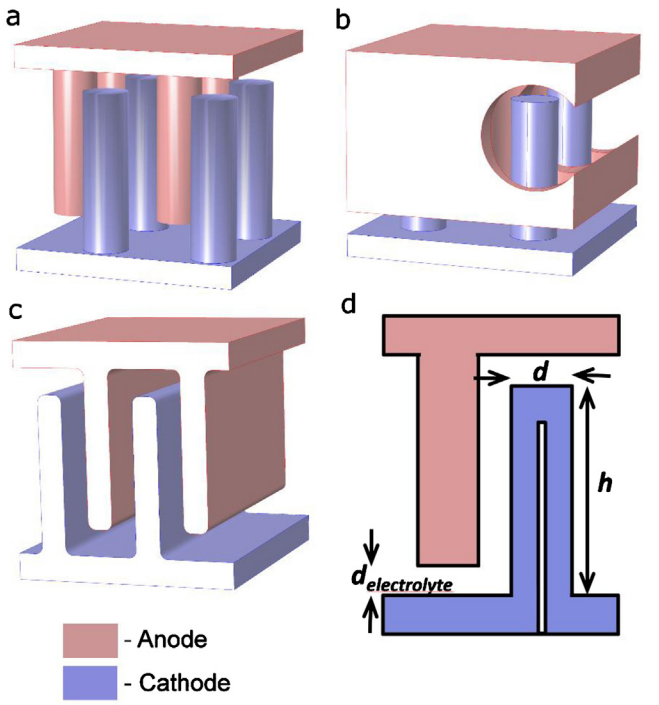

Fig. 1. Investigated 3D microbattery architectures: a) 3D interdigitated, b) 3D concentric with a horizontal cutout to show the internal structure, c) 3D trench. d) A principle schematic side view of all the 3D battery architectures where $d_{electrolyte}$ is thickness of the electrolyte, d is diameter of the electrode pillars/plates and h is height of the electrode pillars/plates during all simulations. All symbols are described in Table 1.

2.2. Electrochemical model

The present study is based on Newman's approach of porous electrode theory and concentrated solution theory for the Li-ion battery [1,42,43]. The mass transport due to the diffusion in the electrolyte originates from Stefan-Maxwell's multicomponent diffusion equation [44]:

$$\varepsilon_{l,i}\frac{\partial c}{\partial t} = \nabla \cdot (D_{i,eff}\nabla c) + \frac{(1-t_0^+)}{F}J \quad (1)$$

where subscript $i = a,c,e$ (corresponding to anode, cathode and electrolyte), $D_{i,eff}$ is the effective salt diffusion coefficient (m^2/s) in phase i of the electrolyte, $\varepsilon_{l,i}$ is the phase volume fraction, c is the electrolyte salt concentration (mol/m^3), J (A/m^3) is the local volumetric transfer current density due to charge transfer, t_0^+ is the Li-ion transport number and F is Faraday's constant. The effective diffusion coefficient is calculated according to Bruggemann's relation $D_{i,eff} = \varepsilon_{l,i}^{1.5}D$. Mass transport in the electrodes is determined by Fick's second law:

$$\frac{\partial c_s}{\partial t} = D_s \cdot \nabla^2 c_s \quad (2)$$