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Microstructure reconstruction and impedance spectroscopy study of $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ Li-ion battery cathodes

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ABSTRACT

Cathode materials have been the focal point of research in the quest for high-performance secondary battery technology in consumer electronics and electric vehicles. The present work investigates the effect of the microstructural morphology of major cathode materials ($LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$) on the performance of the Li-ion battery related to the charge and species transport. Simulated annealing method (SAM) was implemented to generate a virtual 3D domain of the electrode microstructure using a spherical particles, average radius of 3 and 6 μm. An equivalent circuit composed of resistance, capacitance and Warburg impedance was used to model the impedance response of the overall electrochemical reaction occur inside a typical battery system. Electrochemical impedance spectroscopy (EIS) results show that the ionic and electronic mobility in the solid electrode and bulk electrolyte were significantly determined by the morphology of the electrode microstructure. Higher porosity microstructures usually tend to have larger solid-electrolyte interface (SEI) area and lower pore tortuosity which improves the ionic diffusivity in solid and electrolyte phase. Furthermore, the Bruggeman's exponent for effective conductivity and diffusivity was derived from geometrical parameters of the reconstructed microstructure. The real and imaginary parts of the impedance were then presented in Nyquist plot on a frequency range of 20 kHz to 10 mHz.

1. Introduction

Since the first commercialization in 1991, Li-ion batteries become the main power source for many portable devices such as cellular telephones and other electronics. When compared with the more conventional power storage devices such as lead-acid and Ni-Cd, Li-ion batteries provide high working voltage and high specific capacity up to 280 mAh/g [1,2]. The fact that Li-ion battery is regarded as 'green battery' is due to minimized capacity fade over several cycling, lower self-discharge rate (less than 5% monthly) and non-toxicity to the environment [3–5]. Recent hybrid and pure electric vehicles require energy storage system designed to meet prolonged mileage per single charging (high energy density), proper acceleration and torque (high power density), safety operation and lower cost [6–8].

The quest for next-generation Li-ion batteries attract the attention of many researchers and generates a significant number of publications. Despite several efforts, the storage capacity of Li-ion battery improves slowly over the past several years. Limited intercalation dynamics of Li-ions in the active material and slow diffusion process through porous electrode are major capacity restraining factors. The former can be improved through nanosynthesis such as chemical doping while the later can be addressed experimentally via microstructure engineering and numerically through mesoscale modeling of porous electrodes. Essential input parameters for numerical microstructure reconstruction are particle morphology, volume fraction of porosity and two-point autocorrelation function. Specific surface area (electrode-electrolyte interface area) and tortuosity are distinctive parameters derived from the 3D reconstruction. Tortuosity can be expressed geometrically as the ratio of the average pore capillary length between two random points to the geometrical shortest path between the points. Li-ion cathodes have been evolved through various material combinations such as lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), nickel cobalt aluminum (NCA) and nickel cobalt manganese (NCM) proving a wide range of cell voltage capacity, energy density, and cost. Generally, Li-ion battery cathodes are composed of active particles (LCO, LMO, LFP etc.), cathode binders such as polytetrafluoroethylene (PTFE) and polyvinylindene fluoride (PVDF) immersed in an electrolyte solution of lithium hexafluorophosphate ($LiPF_6$).

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The first series of rechargeable Li-ion batteries were first introduced in 1976 by Whittingham [9] that involve TnS_2 as positive insertion electrode and solid electrolyte. However, it is restricted from commercialization due to low cell voltage and the high-temperature environment that this battery requires operating. In 1980, a research group led by Goodenough [10] replaced sodium by lithium and sulfides by metal oxides to develop a new cathode material of $LiCoO_2$ to improve the low cell voltage of sulfide cathodes. The crystal structure $LiCoO_2$ (space group *R-3m:H*) is tetragonal with a layer of lithium and cobalt connected by oxygen molecule that allows the transportation of Li-ions in two directions. The third generation of Li-ion battery cathode material was proposed by Thackeray et al. [11] in 1986 composed of transition metal oxide ($LiMn_2O_4$, space group *fddd:2*), an insertion type with spinel-type structure having lithium extraction ratio as high as 0.6 ($Li_{1-x}Mn_2O_4$ for $0 < x < 0.6$) providing a stable internal spinel structure. Extra lithiation of this cathode material ($Li_2Mn_2O_4$) ensures a wide range of lithium-ion insertion and extraction, thus the theoretical capacity is almost doubled since the number of charge carrier (i.e. Li^+) has doubled. The fourth generation of Li-ion cathode material contains olivine $LiXPO_4$ [12] (where X is Fe, Mn, Ni etc.) having orthorhombic crystal structure (space group *pnma*) that allows transport of Li-ions in one direction. The extraction of lithium from $LiFePO_4$ is possible up to 60% at $0.05\,mA\,cm^{-2}$ vs. 3.4 V with the actual capacity of 100–110 mAh/g. Generally, transition metals exhibit multiple oxidation states that give them special properties of oxidizing agents that tend to accept electrons to become a lower stable oxidation state.

Several strategies have been designed by researchers to improve the performance of Li-ion batteries such as implementing smaller size active particles, modifying the microstructure morphology, chemical doping, electrode coating, and electrolyte chemistry modification. Recent work depicts that, through a systematic engineering of electrode microstructure substantial performance enhancement can be achieved [13,14]. In this paper, we report an EIS model to analyze the inter-microstructural ionic and electronic mobility in active material and electrolyte solution. Simulated annealing method (SAM) based on spherical active particles were used to reconstruct a microstructure domain of the cathode electrodes. We believe that recent advances in the technology of engineered electrode microstructure manufacturing support the viability of our study to achieve the desired performance enhancement of Li-ion batteries.

2. Modeling

2.1. Numerical microstructure reconstruction

Microstructures of common Li-ion cathodes (LCO, LMO, and LFP) were reconstructed numerically using SAM composed of active material (55% and 50% volume), inactive/additive materials such as carbon black and polymeric binder (15% volume) and pore/electrolyte cathode electrode (30% and 35% volume). The domain of the reconstructed microstructures contains 1000000 voxels (100 μm × 100 μm × 100 μm, where one voxel represents 1 cubic μm) and micro-sized spherical particle of mean radius (Ë) 3 μm and 6 μm were agglomerated into the volume until the porosity and two-point autocorrelation function is satisfied. In most Li-ion electrodes, the amount of conductive carbon is limited to 5% [15] by weight or volume. Higher amount of carbon black in the electrodes enhances the electronic conductivity but decreases the ionic conductivity since it fills some micro-pore capillaries. This phenomenon raises the pore tortuosity (τ) of the microstructure and hurdles the ionic diffusivity [16].

SAM is a numerical method inspired by the metal cooling process to form a new crystal structure where a metallic specimen is heated to an elevated temperature and cooled slowly to a room temperature until the global minimum energy state (ground zero equilibrium) is achieved [17]. The probability of a system having an energy state E at any given temperature T is given by Boltzmann distribution [18] as follows:

$$P(\delta E) = exp(-\delta E/T(k)) \quad (1)$$

where k is a small annealing temperature step. The main input physical parameters for the numerical SAM are the size of the reconstructed domain, active particle morphology, porosity (volume fraction of electrolyte, ε_e) and a two-point autocorrelation function obtained from a porous media. More information on SAM is presented in detail elsewhere [19,20].

2.2. Impedance analysis of the ionic and electronic transport

Experimental EIS employs a small perturbation to a steady state system in the form of alternating current or voltage usually over a frequency range of 100 kHz to 10 mHz [21–23]. EIS measurement can be done in galvanostatic (constant current) or potentiostatic (constant voltage) state and the corresponding current or voltage is measured at each frequency step. The ratio of the resulting voltage and current response is the impedance (transfer function). After each perturbation, the time taken for the electrochemical system to reach a new steady state condition (relaxation) given by the product of resistance and capacitance. Faster relaxation time (τ_R) is related to faster electrochemical processes which occurred in high-frequency regions of the impedance spectroscopy. The impedance model used in this work is based on the essence of porous electrode microstructure morphology and its impact on the performance of an electrochemical cell. A typical Li-ion battery as the one shown in Fig. 1, consists of lithiated carbon (L_xC_6) as

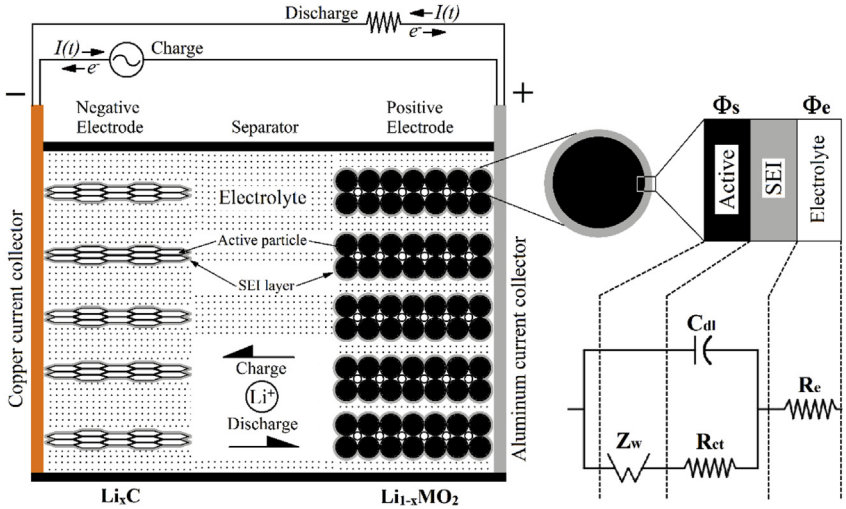

Fig. 1. Schematic diagram of intercalation Li-ion battery (left) and equivalent-circuit diagram of interfaces (right).