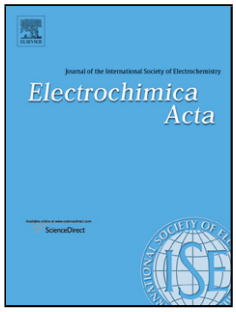

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The influence of point defects on the entropy profiles of Lithium Ion Battery cathodes: a lattice-gas Monte Carlo study

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In-situ diagnostic tools have become established to as a means to understanding the aging processes that occur during charge/discharge cycles in Li-ion batteries (LIBs). One electrochemical thermodynamic technique that can be applied to this problem is known as entropy profiling. Entropy profiles are obtained by monitoring the variation in the open circuit potential as a function of temperature. The peaks in these profiles are related to phase transitions, such as order/disorder transitions, in the lattice. In battery aging studies of cathode materials, the peaks become suppressed but the mechanism by which this occurs is currently poorly understood. One suggested mechanism is the formation of point defects. Intentional modifications of LIB electrodes may also lead to the introduction of point defects. To gain quantitative understanding of the entropy profile changes that could be caused by point defects, we have performed Monte Carlo simulations on lattices of variable defect content. As a model cathode, we have chosen manganese spinel, which has a well-described order-disorder transition when it is half filled with Li. We assume, in the case of trivalent defect substitution (M=Cr,Co) that each defect M permanently pins one Li atom. This assumption is supported by Density Functional Theory (DFT) calculations. Assuming that the distribution of the pinned Li sites is completely random, we observe the same trend in the change in partial molar entropy with defect content as observed in experiment: the peak amplitudes become increasing suppressed as the defect fraction is increased. We also examine changes in the configurational entropy itself, rather than the entropy change, as a function of the defect fraction and analyse these results with respect to the ones expected for an ideal solid solution. We discuss the implications of the quantitative differences between some of the results obtained from the model and the experimentally observed ones.

Keywords: Monte Carlo; ; ; ; ; , manganese spinel, entropy profiling, order/disorder transitions, point defects, solid solution

1. Introduction

The growing demand of rechargeable batteries for electric vehicles and stationary storage not only pushes for higher energy and power density but also improved durability and safety [1–

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