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Lithiation heterogeneities of graphite according to C-rate and mass-loading: A model study

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ABSTRACT

Performance and durability of lithium-ion batteries highly rely on local conditions inside electrodes during operation. In this paper, local physical conditions inside a standard graphite electrode are explored at various C-rate and mass-loading with a physic-based model, validated with electrochemical experiments.

The typical equilibrium potential curve of graphite controls strongly the intercalation heterogeneity along thickness and this heterogeneity is maximal for state of charge corresponding to regions of flat equilibrium potential. Indeed, a flat equilibrium potential promotes lithiation disparities along thickness, whereas a variable equilibrium potential enhances a quick return to a homogeneous lithiated electrode. Current and mass loading affect proportionally these heterogeneities, which are linked with a decrease in cell performance. A correlation between heterogeneities and equivalent resistances interpolated from galvanostatic discharge is found. Pathway resistances calculated from simulation outputs indicate preferential locations of intercalation under operation, depending on the difference between the local and global equilibrium potential of the graphite electrode.

1. Introduction

Nowadays, lithium-ion batteries (LIB) are largely widespread [1], equip more and more electrical portable devices and are foreseen as the next energy sources for personal vehicles. This growing demand required improvements in both energy density and reliability, which are quite challenging and demand an intensive research on novel material [2]. Another way to increase batteries performance and durability relies on optimization of its different components with current materials [3–5].

In most cases, negative electrodes of LIB are made of graphite. Introduced in the 90s, graphite used as an insertion material in lithium cell presents a good reversible intercalation of lithium with good structural and interfacial stability, good electronic properties, a specific capacity of 372 $mAh.g^{-1}$ and a low operating potential [6]. All these properties make graphite a reliable active material for negative electrodes of LIB.

This material is well-known for LIB application, but a full understanding of its kinetics during operation remains challenging, and is necessary for optimization purposes. Experimental validations of hypotheses face difficulties when it comes to measure local physical variables for an electrochemical system in operation. Development of neutron diffraction technics can provide information on local state for various state of health [7,8], but remain complex and costly.

Appropriate mathematical models validated with experimental and representative results are another powerful tool to provide predictions of the internal behavior of battery cell [9–11] or ageing mechanisms [12–14]. Moreover results of such models can be compared to local *operando* measurements and provide guidance for the development of new techniques.

Performance and durability of LIB highly depend on the local conditions inside electrodes during its operation [3]. An inhomogeneous current distribution in a lithium-ion cell can dramatically

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decrease capacity performance. For example, Zhang et al. show experimentally that a non-uniform lithiation occurs during fast discharge which contributes to an under-utilization of active material [15]. Local conditions also affect durability, as observed by Burow et al. [16] who reported an inhomogeneity of graphite degradation under low temperature pulse cycling conditions. They attribute the origin of degradation heterogeneities to the temperature and salt concentration gradient inside the cell. The objective of this study is to investigate local heterogeneities inside graphite electrodes depending on mass-loading and C-rate with a mathematical model. The reliability of the analysis requires a validated model. Therefore, global electrochemical experiments of representative graphite electrodes have been performed to build and validate a physic-based mathematical model, to finally qualitatively predict and analyze local conditions inside the electrodes under operations.

In the first part of this article, experimental achievements are described. Galvanostatic discharges of lithium-graphite coin cells are conducted for different mass-loadings and C-rates. In the second part, a mathematical model based on Newman's approach [10,17–19], is developed and a fitting procedure on a minimum set of lithiation experiments is presented to determine the unknown and most critical physical parameters of the model. Indeed, instead of deducing experimentally a maximum amount of physical parameters [9], or adjusting all of them, which is time consuming, a sensitivity analysis has been performed to determine which parameters have the strongest influence on the model.

In a third part, simulation results are analyzed to get insights on the impact of active material loadings and C-rates on intercalated lithium heterogeneities in graphite electrode during operation. A mechanism is proposed for the description of heterogeneous lithiation inside graphite electrode. Lithiation heterogeneities during operation are also correlated to interpolated global resistances extracted from experimental results. Furthermore, internal electrode resistances are decomposed at various electrode depth and state of charge to better apprehend the origin of the heterogeneities.

2. Experimental

The studied graphite coin cells consist of a metal lithium sheet on an aluminum collector, two Celgard 2400 separators, and a graphite-based electrode on a copper collector. Three graphite electrodes have been manufactured considering three different loadings of 5.67, 7.85, and 11.96 mg cm^{-2}, respectively named W_1, W_2, and W_3 in the following. The porosity has been controlled during the manufacturing process to ensure a same value to all the electrodes. Therefore, only their thicknesses differ and are directly correlated to their respective mass loading. The electrodes contain 96 wt% of SLP30 graphite powder from Timcal. The electrolyte consists of 1 M of lithium hexafluorophosphate ($LiPF_6$) in 1:1:1 weight proportion of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC). Graphite electrodes are 16 mm in diameter. After assembly, a formation protocol is applied to the coin cells. Two cycles of full lithiation/delithiation are applied between 0 and 1.6 V at C/10 to get good solid electrolyte interface (SEI) properties. All the electrochemical measurements on coin cells were performed using a modular potentiostat/galvanostat/EIS VMP3 from Bio-Logic, Claix, France. Ambient temperature remains at 20 °C.

After the formation protocol, coin cells were lithiated at various currents from 0.1 to 5C, always after a complete delithiation at C/10, without constant voltage phase. Experimental capacities of the 3 different coin cells are given after formation cycles by measuring the capacity on the first C/10 lithiation curve. Capacities reach 2.93, 4.15, 6.43 mAh for loading W_1, W_2 and W_3 respectively. It corresponds to specific capacities at respectively 336, 343 and 349 mAh/g. The specific capacity increases with increased mass loading, but due to the non-uniformity of collector coating during electrode synthesis, this tendency is not relevant. Indeed, mass loading deviation on the electrode fabrication process reaches 3.5%, 4% and 5% (0.2, 0.3 and 0.6 mg cm^{-2}) of mass loading W_1, W_2 and W_3 respectively. The graphite powder SLP30 has been observed on SEM. On Fig. 1, the typical shape of this graphite powder is shown as can be found in Ref. [20]. Graphite particles appear as flakes or flat cylinder.

Separator and electrolyte conductivity measurements have been made on coin cells composed of electrolyte, with or without one Celgard 2400 separator, between two aluminum current collectors, without electrodes. The separator conductivity or the electrolyte conductivity at prescribed salt concentrations are extracted from impedance spectroscopy measurements carries out on the respective coin-cells [21]. These values are used to determine the MacMullin number of the separator, defined as the quotient of electrolyte conductivity over the separator conductivity. This number, N_m, is characteristic of the separator microstructure, and independent of the salt concentration [22]. With the knowledge of electrolyte's conductivity κ at different salt concentrations and the MacMullin number, N_m, the variation of the separator conductivity through a wide range of salt concentration can be given by:

$$\kappa^{eff} = \frac{\kappa}{N_m} \tag{1}$$

To characterize the lithium foil, a double lithium-lithium coin-cell with two Celgard 2400 separators has been assembled and several steps of current have been applied. Current-Potential curves of lithium electrodes are thus measured. The exchange current of the lithium electrode is extracted from this curve using a linear approximation of the Butler-Volmer equation. The obtained value of 10 A m^{-2} agrees with the value of 5.5 A m^{-2} found in Ref. [23] where a solid electrolyte was used which could explain the difference to a lower value.

3. Theory

3.1. Mathematical model

A physic-based model choice has been preferred in order to approach the local physics of graphite electrode. The model used in this work is based on the theory of porous electrodes originally introduced by Newman and Tiedemann [19] and developed

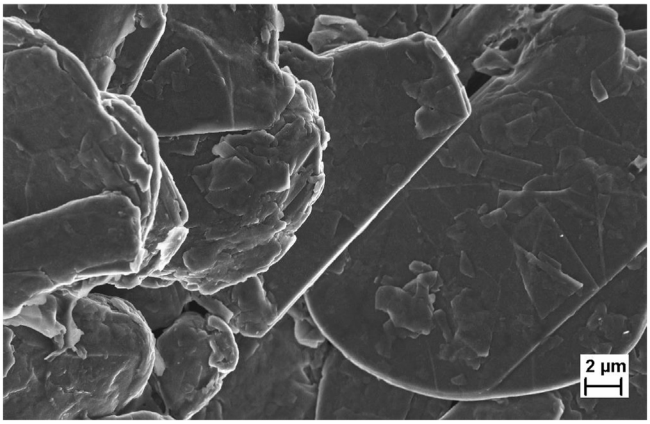

Fig. 1. MEB measurement on SLP30 Graphite from TIMCAL.