



Interpreting Lithium Batteries Discharge Curves for Easy Identification of the Origin of Performance Limitations



Renaud Cornut¹, David Lepage, Steen B. Schougaard*

NanoQAM research center, Department of Chemistry, Université du Québec à Montréal, 2101 rue Jeanne-Mance, post 3911, Montreal

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ABSTRACT

A simple method is proposed to interpret limited discharge performances of composite positive electrodes in terms of charge transport in the electrolyte vs. charge transport in the active material.

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1. Introduction

A common approach to ensure high energy density and chemical reversibility in rechargeable batteries is to employ solid-state materials amiable to alkali ion insertion reactions [1–3]. The insertion reaction however has several drawbacks, such as, the transport of ions inside the solid is slow compared to transport in liquid electrolytes. To overcome this problem, the electrodes employed in insertion batteries consist of active material in micron to nanometer sized particle form mixed with additives like polymeric binder and carbon. This solid matrix is porous, so that the liquid electrolyte may penetrate deep inside the electrode. Consequently, the electrode has considerable structural complexity, which makes analyzing performance challenging. *E.g.* a common problem is to identify if the performance is limited by transport in the liquid electrolyte part of electrode or by transport in the active material particles [4].

The problem of charge transport and electrochemical performance of composite electrodes has previously been examined theoretically. As such, empirical methods based on a careful comparison of the discharge characteristics of several materials have lead to models with analytical solutions [5–7]. They have the advantage of simplicity, with the trade-off of limited validity range.

More complex and accurate models, able to reproduce entire discharge curves have also been developed [8–13]. These necessitate an expertise in numerical simulation and more importantly, they require the knowledge of many parameters characterizing the system under study, including electronic and ionic conductivities, size of the particles, porosity *etc.* Consequently extensive characterization of the electrode and its components is required to employ these models. In the present study the simplicity of the empirical methods and the accuracy of the numerical studies are combined to derive a simple technique for identification of the factor limiting the performances of a positive electrode. In addition, the analysis allows for the evaluation of the associated transport parameters.

2. Experimental

2 g of LiFePO₄:poly(3,4-ethylenedioxythiophene) composite, pedot-LiFePO₄ hereafter, prepared according to ref. [14] was mechanically mixed with 4 g of a solution of 3% (w/w) PVDF (Kynar[®] KF Polymer W#1100) in *N*-methylpyrrolidone (Aldrich). The suspension was coated onto carbon coated Al foil (Exopack #2651) with a micrometer adjustable film applicator (MTI corp.). The applicator was adjusted to various thicknesses to yield coatings 1 to 4. The coatings were subsequently dried at 60 °C for three hours in ambient air and under vacuum overnight. After this drying the thickness of the active materials was measured using a micrometric head (Mitutoyo). The electrodes were transferred to an Argon atmosphere glove box (H₂O < 1 ppm, O₂ < 1 ppm) for coin cell assembly. An 1 M LiPF₆ in a 1:1 ethylene

* Corresponding author. Tel.: +1 514 987 3000; fax: +1 514 987 4054.

E-mail address: schougaard.steen@uqam.ca (S.B. Schougaard).

¹ Present address: CEA-Saclay, IRAMIS/NIMBE/LICSEN, Gif sur Yvette, 91191, France.

carbonate and dimethyl carbonate (Novolyte Technologies) solution served as electrolyte, while the anode and separator consisted of metallic lithium (99.9%, 0.75 mm thick and 19 mm wide; Alfa Aesar) and Celgard 2500 membranes, respectively. All batteries were cycled between 2.2 and 4 V for five cycles at C/5, for stabilization using an 8Channels Battery Analyzer (MTI corp. 0.002–1 mA), prior to the cycling at different C-Rates (2.2–4 V) using a Bio-Logic VMP3 multipotentiostat. Degree of Discharge (DoD) refers to the capacity relative to the maximum capacity at the lowest measured rates. Approximate particle size was determined by examining transmission electron micrographs obtained from a Jeol JEM-2100F TEM operating at 200 kV.

3. Calculations

The partial differential equations systems (see supporting information) were solved numerically using the finite elements method implemented in the commercially available software Comsol version 3.5a. The maximal size of the mesh was set to 0.001 and 0.01 for 1D and 2D domains, respectively, and the relative tolerance was fixed at 10^{-4} . Numerical resolutions lasted few seconds using Quad CPU 2.5 GHz Intel Processor with 8 GB of RAM.

4. Results and discussion

The discharge curves measured for four different electrode coatings based on the same active material, *i.e.* LiFePO₄ with identical chemical composition are presented in Fig. 1. They however differ by their porosity and thickness as indicated in Table 1.

The current density is referenced to the C-rate, *i.e.* the inverse of the discharge time (in h) required to extract the full theoretical capacity of the system. As apparent from Fig. 1, for a given C-rate the Degree of Discharge (DoD), *i.e.* the accessible fraction of the

maximal capacity, strongly depends on the coatings physical parameters, *e.g.* at the 10C-rate the capacity varies from 40 mAh/g for the coating 1 to less than 5 mAh/g for the coating 4. Since the composition is the same for the four coatings, this is a clear indication that the charge transport in the electrode structure, which here includes the electrolyte, strongly influences the performance.

To what extent the electrode structure is limiting compared to the active material is however difficult to identify from the data presented Fig. 1. In contrast, we have found empirically that plotting $1/DoD$ as a function of C-rate leads to a linear behavior at low rates for electrodes expected to be limited by the transport in the active particle (high porosity, low thickness) (Fig. 2).

Our analysis was extended to insertion battery system data from the recent literature selected at random (see supporting information) [15–17]. Surprisingly, the same linear behavior is found at low C-rates over a wide range of systems, provided that the voltage cut-off window is sufficiently large to provide the sharp decrease of potential at the end of charge, as is the case in Fig. 1.

To explore this behavior in depth, numerical simulations were employed. Using the same approach as adopted by Newman et al., we considered the electrode as the macro-homogeneous superposition of two media transporting the electronic and ionic charges, in addition to the transport of inserted ions inside the active material particles [18–20]. The corresponding equation system is presented in the supporting information section. Importantly, while it has been shown previously that the microscopic mechanism for lithium uptake and release is remarkably complex for the Li_{1-x}FePO₄ system [21–28], we here use a spherical diffusion model to describe lithium transport, as recent data suggests that this yield correct kinetic predictions within the experimental error for the oxidation process [29]. The numerical investigation of a wide range of model parameter combinations, followed by the careful analysis of the resulting discharge curves lead to the conclusion, that two unique sets of

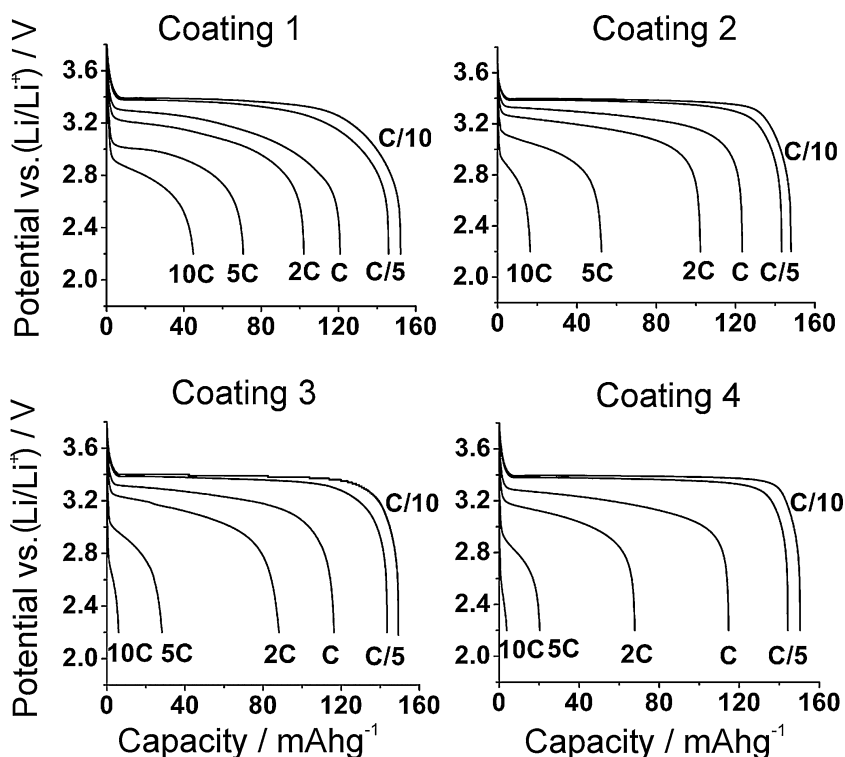


Fig. 1. Experimental discharge curves for different C-rates. (For thickness and porosity see Table 1. Chemical composition: 80–85 wt-% LiFePO₄, 10–13wt% poly(3,4-ethylenedioxythiophene) and polyvinylidene difluoride.

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