

Internal dynamics of blended Li-insertion electrodes

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ARTICLE INFO

Keywords:

Blended electrodes

Internal dynamics

Pulse

Relaxation

ABSTRACT

The blending of different Li-insertion compounds is a successful concept to tailor the properties of electrodes for Li-ion batteries. Recent own studies and reports from literature suggest internal redox processes that do not occur in electrodes consisting of a single type of active material. Herein, we summarize recent electrochemical experiments along with theoretical considerations related to internal dynamics in blended insertion electrodes. A special experimental setup and a model-like blend electrode is applied to capture any interactions among the constituents of the blend. In accordance with theoretical considerations from the literature, it is shown experimentally that the constituents are charged/discharged independent from each other, which can lead to high effective C-rates for an individual constituent. At high loads, a constituent with fast reaction kinetics can act as an internal pathway, carrying the current for a more rate-limited constituent. This effect enables very good rate capability but also includes multiple reaction steps, which might reduce the cycle life performance. Furthermore, it is shown that changes in temperature induce a redistribution of Li among the constituents without any active cycling of the cell. These recent insights regarding internal dynamics are discussed with respect to beneficial and unfavorable impacts on the performance of Li-ion batteries with blended insertion electrodes.

1. Introduction

At the present day, Li-ion batteries (LIBs) are widely used in portable consumer electronics and become increasingly attractive in the automotive industry [1–3]. However, enabling the broad adoption of secondary batteries in the transportation sector still requires the improvement of cost efficiency, lifetime, safety and electrochemical performance [4,5]. Current electrodes for LIBs base on transition metal oxides with layered structure (e.g. LiCoO₂ [6]), spinel structure (e.g. LiMn₂O₄ [7]) or olivine type compounds (e.g. LiFePO₄ [8]). These Li-ion insertion hosts were intensively explored and effectively applied to the construction of commercial LIBs. The layered materials are typically considered as positive electrodes for high-energy systems [9]. Spinel and olivine type materials are usually applied in the case of high-power applications or because of their low cost [10].

The blending of Li-ion insertion compounds is a promising approach to build advanced electrodes for LIBs [11]. The active element of a blended electrode is a mixture of different Li-ion insertion materials (Fig. 1). Mixing of different insertion materials such as blends of layered-layered [12], layered-spinel [13–16], layered-olivine [17,18] and spinel-olivine [19,20] compounds is done very successful to compensate individual disadvantages of the pure materials, e.g. regarding

safety [12,13], rate capability [21,22] or cycle stability [14–16,23]. Accordingly, blended insertion electrodes have attracted intense attention in the research community. However, some basic interactions between the constituents of a blended electrode and differences towards common electrodes, consisting of a single type of insertion material, have hardly been studied so far.

Recent fundamental research on the behavior of blended insertion electrodes suggests internal redox processes in blended electrodes that do not occur in electrodes consisting of a single type of active material. Theoretical considerations of Tran et al. suggest that the constituents of a blend can be charged/discharged individually, depending on their specific redox potentials [13]. Huang et al. propose that, after a temperature change, the transient open circuit potential of a blended electrode is actually a mixed potential, which should drive a balancing current among the constituents [24]. Gallagher et al. suggest that a constituent with fast kinetics can act as an internal redox couple to charge and discharge a more rate limited constituent at high loads and subsequent relaxation [18]. This effect was also observed in simulations of the galvanostatic intermittent titration technique carried out by Mao et al. [25].

However, the detailed investigation and quantification of such effects is a sophisticated experimental challenge since the typical particle

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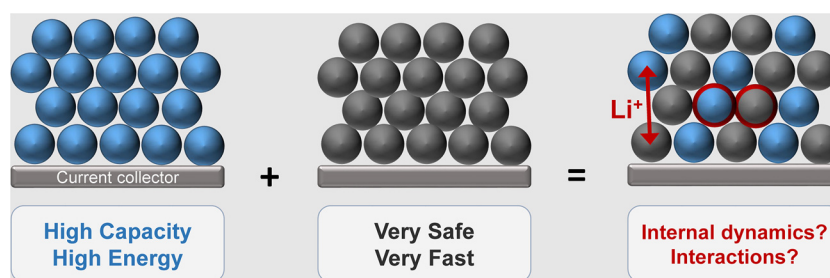


Fig. 1. Schematic drawing illustrating the principle of blended insertion electrodes and the objective of the present work.

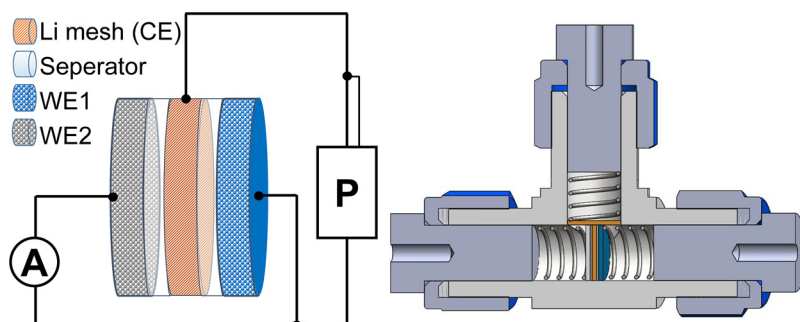


Fig. 2. Schematic illustration of the experimental arrangement. The two shorted working electrodes, WE1 and WE2, face each other, separated by porous, electron blocking separators soaked with electrolyte. A lithium net in the center of the cell forms the counter electrode (CE). This setup is implemented into a T-type Swagelok® cell. The ammeter (A) measures the short circuit current between WE1 and WE2 during electrochemical experiments conducted via the potentiostat/galvanostat (P).

size of insertion materials is in the sub-micron range. To gain fundamental insights into the internal dynamics of blended insertion electrodes and to investigate the effects proposed in the literature, we developed a special experimental setup including a model-like blend electrode that allows capturing any electrochemical interactions among the constituents of the blend.

The experimental setup was described in detail in a previous paper [26]. In brief: in a fully intermixed blended insertion electrode, the different active material particles are short-circuited by direct physical contact, via the conductive additives or the current collector foil. From the thermodynamic point of view, this situation is identical to multiple electrodes shorted with a low-impedance connection. Based on these considerations and inspired by techniques from bimetallic corrosion investigations, we form a model-like blend electrode by using two separate but short-circuited insertion electrodes (cf. Fig. 2). In the cell, two shorted working electrodes face each other, separated by two porous membranes with a Li net in between as the counter electrode. If a voltage or current (I_{total}) is applied to the cell, the measurement of the short circuit current (I_{WE2}) allows to separate the electric charges that are consumed by the individual constituents according to:

$$I_{\text{total}} = I_{\text{WE1}} + I_{\text{WE2}} \quad (1)$$

Furthermore, during open circuit measurements ($I_{\text{total}} = 0$), the short circuit current indicates any balancing effects among the constituents.

Herein, we summarize our recent insights regarding internal dynamics in blended insertion electrodes obtained by using model-like blend electrodes. The results gained and recent reports from the literature are discussed regarding beneficial and unfavorable impacts on the performance of Li-ion batteries with blended electrodes.

2. Experimental

Electrochemical experiments were carried out using the cell arrangement shown in Fig. 2. A potentiostat/galvanostat with integrated frequency response analyzer (VMP3, Biologic) was used to apply a

desired cell voltage or current. Simultaneously, the short-circuit current between the two working electrodes was measured by a 2100 6.5-Digit USB Digital Multimeter (KEITHLEY).

The electrodes investigated in this study were received from a commercial supplier (MTI Corp.). They were made of active material (either LiFePO_4 , $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, LiCoO_2 or LiMn_2O_4), binder (polyvinylidene fluoride) and conductive additive (carbon black) coated on an aluminum current collector. Additional information on the electrodes and active materials are available as Supplementary material.

Electrochemical cells were assembled in an argon-filled glove box ($< 5 \text{ ppm H}_2\text{O}$, 5 ppm O_2) as follows. Two short-circuit electrodes were used as the working electrode (cf. Fig. 2). A net of metallic Li served as the counter electrode (99.9% trace metal basis ALDRICH Chemistry). High purity 1 M LiPF_6 solved in a 1:1 wt% ratio mixture of ethylene carbonate and diethyl carbonate acted as the electrolyte (ALDRICH Chemistry). The model-like blend electrodes were cycled until stable conditions had been achieved. Afterwards, several electrochemical techniques were applied to the cell, which are described at the relevant position in the following sections.

3. Results

3.1. Individual redox behavior

The individual charging and discharging of the constituents in a blended electrode was studied using the example of a 1:1 wt% mixture of LiCoO_2 and LiFePO_4 [26]. This corresponds to a theoretical capacity ratio of $Q_{\text{LiCoO}_2} : Q_{\text{LiFePO}_4} = 0.9$. Fig. 3 depicts a cyclic voltammogram (CV) of the model-like blend measured at a low scan rate of $25 \mu\text{V s}^{-1}$. Positive currents are associated with Li-extraction from the blend and negative currents indicate Li-insertion. In the anodic sweep, two oxidation peaks are observed at approximately 3.7 and 4.1 V. In the following cathodic sweep, two corresponding reduction peaks emerge at approximately 3.25 and 3.6 V. The experimental setup allows us to

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