



Short Communication

Analysis of the counter-electrode potential in a 3-electrode lithium ion battery cell

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ABSTRACT

A phenomenon which was not yet described is observed in the potential course of a lithium metal counter electrode (CE) employed for investigations of porous graphite electrodes (WE). The potential characteristics of the CE were found to be strictly connected to the lithium concentration in the active material of the WE. The authors suggest that the observed phenomena at the CE are related to changes of the current density distribution across the thickness of the porous WE. The local depletion/enrichment of lithium in the pores affects the lithium concentration gradient in the electrolyte which results in changes of the overpotential at the CE. This relation may be used prospectively to study the current density distribution in porous electrodes as a function of time, C – rate and state of charge.

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1. Introduction

Lithium metal is used as counter electrode (CE) in lithium ion battery research for decades in order to study porous electrodes, electrolytes and their interactions [1]. Thereby, a 3-electrode configuration is used for detailed investigations of the kinetics, excluding any influence of the CE. In a 3-electrode configuration the CE and the working electrode (WE) form a circuit over which the current is either applied or measured. The potential of the CE is adjusted by the potentiostat/galvanostat to balance the reaction rate (current) at the WE [2]. The potential of the CE is usually not analyzed. However, the authors found a highly reproducible phenomenon in the potential course of the lithium metal CE used for investigations on porous graphite electrodes which was not yet described in literature. The potential course of the CE significantly deviates from the behavior expected during stationary lithium dissolution and deposition, respectively. Furthermore, the potential of the CE was found to be strictly related to the lithium concentration in the active material of the WE. In this communication, the observed phenomenon and an explanatory approach are presented.

2. Experimental

The graphite electrodes were composites of 94 wt.% graphite (SLP 10, Timcal), 1.88 wt.% carbon black (SuperP, Timcal) and 4.21 wt.% binder (styrole butadiene rubber/sodium carboxymethyl cellulose in ratio 4.69: 1) on a 10 μm copper current collector. The electrodes were

produced by tape casting of a water based slurry. Subsequently, the porosity was set to 33% by calendaring with a force of 1 kN mm⁻¹. The thickness of the electrodes amounted to approximately 35 μm. The electrochemical experiments were carried out in 3-electrode Swagelok® cells. The graphite foil was the WE, the CE was a circular lithium foil (MaTeck, 99.8%) with a diameter of 1.27 cm². As reference electrode the tip of a lithium metal wire (MaTeck, 99.8%) was placed between two layers of separator peripherally at the electrodes. Thus, all potentials are given versus Li/Li⁺. Commercially available high purity 1 M LiPF₆ in ethylene carbonate: diethyl carbonate in a 1:1 weight ratio was used as electrolyte (Selectilyte™ LP40, BASF). The separator was a polypropylene non-woven fabric (Viledon® separators, Freudenberg). The assembly of the cells was carried out in an argon filled glove box (Jacomex). For the electrochemical experiments a multi-channel potentiostat – galvanostat with integrated frequency response analyzer (VMP3, Biologic) was used. The cells were subjected a constant current procedure as formation. Subsequently the graphite electrodes were cycled with a constant current of 0.4 mA cm⁻² in a potential range of 0–1 V.

3. Results and discussion

Fig. 1 shows the measured course of electrode potential of the graphite WE, E_{WE} , as a function of the lithium concentration in the active material during lithiation and delithiation. As expected, the typical plateau regions of graphite are observed [3]. Besides the potential of the WE, Fig. 1 shows the electrode potential of the lithium CE, E_{CE} , during this constant current experiment. According to literature, the potential of the CE is expected to become constant during stationary electrochemical lithium dissolution and deposition [4]. Indeed, quite

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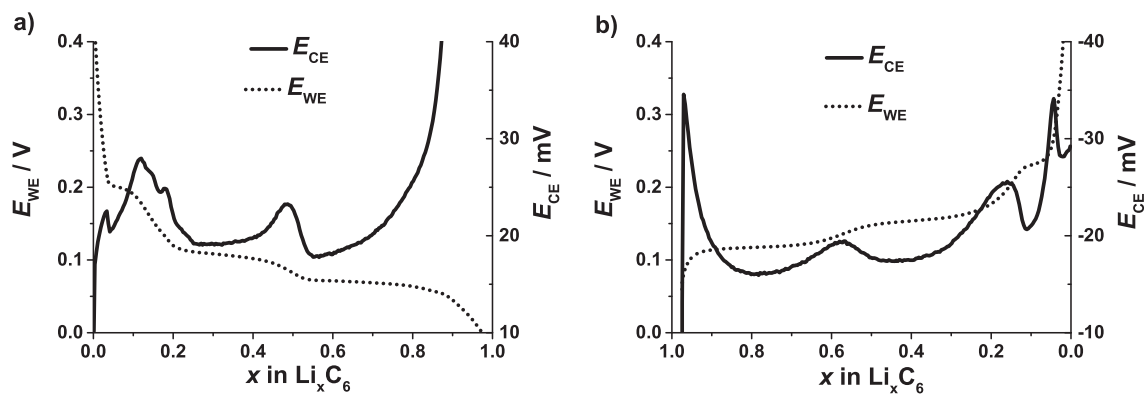


Fig. 1. Electrode potentials of the graphite WE during a) lithiation and b) delithiation, and the lithium CE during a) lithium dissolution and b) lithium deposition.

the contrary, E_{CE} shows a complex characteristic in the course of the experiment which appears to be related to the potential course of the graphite WE.

Literature describes various reversible phase transformations in the course of lithium intercalation into graphite, associated with changes in stage, in-plane and through-plane ordering of the lithium ions in the host material [5,6]. The most important phase transitions during intercalation are marked in Fig. 2a. The two phase regions related to the phase transitions *Stage1L* → *Stage4L* ($0.05 < x < 0.12$), *Stage2L* → *Stage2* ($0.25 < x < 0.5$) and *Stage2* → *Stage1* ($0.5 < x < 1.0$) are obvious as plateaus in the potential curve. Further phase transitions between *Stage4L*, *Stage3L* and *Stage2L* are less distinct and thus still under debate [6–8]. Explicit single phase regions are $0.12 < x < 0.13$ for *Stage4L* and $x = 0.5$ for *Stage2*, being inflection points in the potential course. As a consequence, the derivative of E_{WE} with respect to x is a sensitive indicator for phase transformations of graphite. A plot of the derivative of E_{WE} displays any two phase region as a minimum, whereas single phase regions are maxima (Fig. 2b).

In order to reveal any correlations between the CE and the WE, E_{CE} is comparatively plotted versus the derivative of E_{WE} (Fig. 3). Obviously, the curves exhibit a number of identical features. The distinct accordance between E_{CE} and the derivative of E_{WE} proves that the potential characteristics observed at the CE are in basic relationship to the lithiation/delithiation of graphite and the associated phase transitions. Furthermore, the observed features of E_{CE} as a function of x in Li_xC_6 are not merely valid for one specific graphite electrode, but rather absolutely reproducible for a number of investigated electrodes.

At a first glance, the observed phenomena may appear to be related to capacitive effects as the potential of the CE shows maxima when the potential of the WE changes (cf. Fig. 3). However, this hypothesis does not hold for the following reasons. First of all, the changes of potential of the WE are mainly determined by changes of the equilibrium

potential which depends on the composition of Li_xC_6 [5,6]. The double layer capacitance hardly varies with the composition [9]. Consequently, once the double layer is charged at the very beginning of the measurement, the occurrence of capacitive effects is negligible. Furthermore, the time constant related to the charging of the double layer is in the range of milliseconds. By comparison, the experiments in Fig. 1 last approximately 4 h. Finally, we calculated the capacitive currents at the CE during the experiments in Fig. 1 by using the relation:

$$j_c = C_{dl} \frac{dE_{CE}}{dt} \quad (1)$$

and a typical double layer capacitance of $C_{dl} = 20 \mu\text{F cm}^{-2}$. Capacitive currents were found to be in the nA – range or less than 0.0001% of the applied current. Consequently, capacitive effects can be neglected and the measured electrode potential of the CE is determined by:

$$E_{CE} = E_{CE}^0 + \eta \quad (2)$$

with E_{CE}^0 and η being the equilibrium potential with respect to the RE and the overpotential. As the RE consists of metallic lithium, all deviations from 0 V vs. Li/Li^+ are exclusively determined by the overpotential. The measured overpotential can be separated according to different transport phenomena:

$$\eta = \eta_{\Omega} + \eta_{ct} + \eta_D \quad (3)$$

with η_{Ω} , and η_{ct} and η_D being the ohmic potential drop, the activation overpotential and the diffusion overpotential. Any of these parts depend on the lithium concentration, c_{CE} , in front of the CE [10]. In particular the overpotential related to mass transport limitations, η_D , is a sensitive

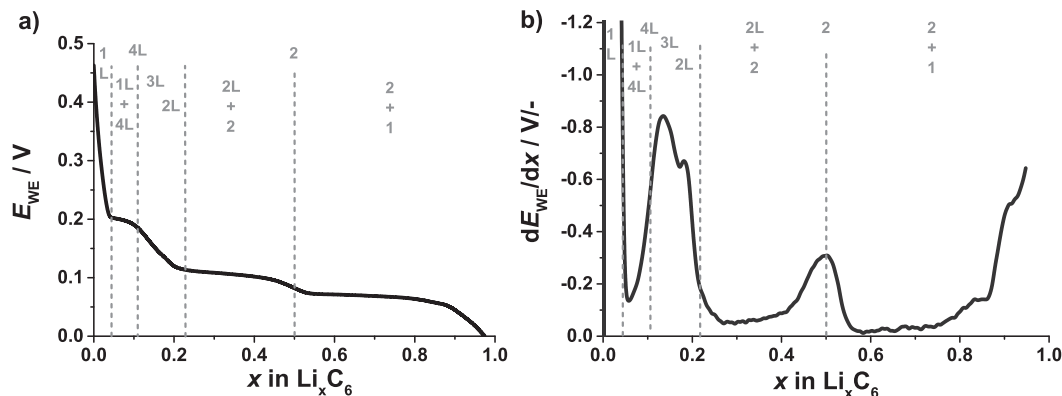


Fig. 2. Different stages and stage transitions of Li_xC_6 and a) electrode potential during lithium intercalation, b) derivative of E_{WE} with respect to x in Li_xC_6 .

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