Electrochimica Acta 207 (2016) 218–223

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Myth and Reality about the Origin of Inductive Loops in Impedance Spectra of Lithium-Ion Electrodes — A Critical Experimental Approach

Harald Brandstätter, Ilie Hanzu, Martin Wilkening*

Graz University of Technology (NAWI Graz), Institute for Chemistry and Technology of Materials, and Christian Doppler Laboratory for Lithium Batteries, Stremayrgasse 9, A-8010 Graz, Austria

ARTICLE INFO

Article history:
Received 25 February 2016
Accepted 22 March 2016
Available online 3 May 2016

Keywords:
Impedance spectroscopy
Lithium-ion batteries
Inductive loops
Negative capacitance effect

ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) is a sophisticated analyzing tool in battery research. Though, there are still phenomena subject to speculation. As an example, for a long time the formation of the so-called Solid Electrolyte Interphase (SEI) has been made responsible for inductive loop formation in impedance spectra. In our opinion, there are, however, no satisfying evidences supporting this attempt to explain the occurrence of inductive loops. The present study is, thus, aimed at answering the question whether other origins such as cell design ought to be considered to reveal the electrical sources for this phenomenon. Therefore, two commonly used anode materials for lithium-ion batteries were investigated with respect to their tendency to the formation of SEIs. Besides the influence of the SEI on the overall impedance response, also the impact of the cell design on electrical response was investigated. We identified four different sources of (i) *inductive* and (ii) *negative capacitance* loop formation: springs, reference electrodes, drift, and corrosion. In conclusion, any interrelationship between inductive loops and SEI formation could be ruled out. This finding disproves an earlier, commonly known attempt that traced the presence of inductive loops back to the formation of passivating surface layers because of electrolyte decomposition.

1. Introduction

The development of advanced electrochemical energy storage systems, which are based on Li ions as charge carriers, is more important today than at any time before [1]. Depending on the active materials chosen, the design of Li-ion batteries may require the formation of passivating films or interphases on those electrodes that operate outside a certain electrochemical potential window. These passive layers are known to be lithium-ion conductors while being electronic insulators. Because of their electronically insulating nature the growth of the film may, in favorable conditions, become a self-limiting process. This means the growth rate of the film is expected to significantly reduce during battery operation, thus, avoiding further electrolyte degradation at the electrodes.

Both positive and negative electrodes are known to form passive films, although the interphases are different in composition and relative stability. The passivating layers at the negative electrode – note that graphite is the most common negative electrode material – are better defined and more stable than those that build up at the positive electrodes. This Solid Electrolyte Interphase (SEI) has been made responsible for the appearance of significant inductive loops in Electrochemical Impedance Spectroscopy (EIS) [2]. The present paper is aimed at revisiting the question whether SEI formation is indeed responsible for inductive loop behavior as seen many times in impedance spectroscopy on lithium-ion cells. Exemplarily, inductive loops were found in EIS studies by Zhuang *et al.*; the authors investigated positive electrode materials such as layered $LiCoO_2$ (LCO) [3] and spinel-type $LiMn_2O_4$ [3].

An inductance is defined as the property of an electric circuit to cause an electromotive force as a result of a change in the current passing through the circuit itself. Gnanaraj *et al.* [4] suggested that inductive loop formation might be explained by the formation of an electromotive force superimposing the process of lithium ion extraction. In the case of layer-structured LCO spatially isolated Li-rich and Li-poor, *i.e.*, Li-deficient, regions may be formed during extraction of the Li ions. Isolation of Li-rich and Li-poor regions in the electrode may, however, also be created by the SEI film due to disequilibrium with respect to electronic continuity. Hence, a concentration cell would be established between the Li-rich domains and the Li-poor regions ($Li_{1-x}CoO_2$, $0 < x < 0.5$) separated by the SEI film. Because the SEI film is imperfect at the early stages

---

* Corresponding author.
E-mail address: wilkening@tugraz.at (M. Wilkening).

http://dx.doi.org/10.1016/j.electacta.2016.03.126

of delithiation of LCO, a current may flow within the concentration cell. This current would generate a field in opposite direction to the field corresponding to lithium ion extraction. Considering the overall discharging and charging processes of an electrode, such a situation would, indeed, provide the requirements for the formation of an inductive loop, as it is explained by the commonly proposed theory. The question arises whether we could really trace back the inductive loop behavior to such local phenomena inside the electrodes. Alternatively, geometric effects, wiring or cell configurations, *i.e.*, macroscopic origins, may serve as much simpler explanations. To our knowledge, a systematic study envisaging these origins through EIS and different cell configurations is, however, still missing.

It has to be noticed from the beginning that electromotive forces generated in the way described above always run from a negative to a positive charge and are, therefore, *curl-free*. The existence of electric curls or a time-variant magnetic flux is the essential criterion of induction [5]. In electric fields without induction there are no closed field lines and, thus, the circulation of the electric field strength is always zero, see equation (1):

$$V_{\mathrm{ind}} = \oint_C \vec{E} \cdot d\vec{r} \overset{!}{=} 0, \tag{1}$$

where V_{ind} is the voltage induced, $\vec{E}$ denotes the electric field strength and $\vec{r}$ the path. Expressed in a simpler way, an inductance L necessarily implies the existence of a magnetic energy storage [6,7].

Interestingly, Hyung-Man Cho *et al.* [8] observed the emergence of an inductance in their semi-empirical equivalent circuit model developed for aged LCO cells but the origin of this feature has yet to be determined. While the influence of cell geometry has been well studied for solid electrolytes and fuel cells, little of this knowledge has been used to explain similar effects in lithium-ion batteries [9]. Swagelok-type cells are rather unreliable for EIS for several reasons. For example, the fact that several equipotential surfaces are probed at once by the reference electrode makes a reliable interpretation difficult. Moreover, unintended electrode misalignments are likely that also complicate the explanation of results from impedance data recorded on Swagelok-type cells. As a result, a strong scaling effect of the high frequency semi-circle and even a second capacitive loop superimposed on the medium frequencies may be observed. Langklotz and coworkers [10] are currently investigating the inductive loop issue by impedance spectroscopy using LCO and $LiFePO_4$ test cells. They observed an influence of cell design to the measurement result without having identified the origin yet [10]. Our present investigations with LTO and graphite cells are intended to finally shed some more light onto these, in our opinion, *hitherto* unexplained issues.

To study the origins of inductive loop formation in EIS in detail we prepared several lithium-ion half cells with different geometry, electrode configuration and two negative electrode materials that largely differ in SEI formation. While graphite is known to form extended passivation layers because of its low electrochemical stability in Li-based cells with common liquid electrolytes, lithium titanate, $Li_4Ti_5O_{12}$, on the other hand, is characterized by an operating potential well above that of metallic lithium, see., *e.g.*, ref. [11]. The high potential prevents the formation of an SEI [12–19]. The cells were prepared as follows.

2. Experimental

Lithium titanate with a purity of ca. 99 % was obtained from Sigma Aldrich. The grain size of the non-treated raw material was in the μm range and reveals the typical X-ray powder diffraction pattern of spinel-type $Li_4Ti_5O_{12}$. In order to prepare dense electrodes we used ball milling to form an active material that is easily to handle. Nanocrystalline $Li_4Ti_5O_{12}$ was prepared from the microcrystalline source material by ball milling using a high-energy planetary mill (Fritsch, Pulverisette 7). We used grinding beakers made of zirconium dioxide (Fritsch) that were equipped with 180 milling balls (ZrO_2, 5 mm in diameter). The air-tight beakers were filled and unfilled in inert gas atmosphere with less than 0.5 ppm water vapor content to avoid any contact of the samples with air or moisture. To prepare the nano-samples the material was milled for 2 h; the rotational speed of the mill was set to 400 rpm in order to reduce the formation of side products as effectively as possible.

For the preparation of the LTO-based electrode, nano-$Li_4Ti_5O_{12}$ was mixed with conductive carbon particulate matter (Super C 65), binder (Kynar 761); N-methyl-2-pyrrolidone served as solvent. After stirring for several hours the viscous slurry was cast (Dr. Blade method, 100 μm casting gap) onto a thin copper foil and dried in an oven. Electrode disks, 10 mm in diameter, were punched out and, when necessary, further cut for cross-section SEM observations. For the graphite electrodes the raw material was directly mixed in the slurry without the ball-milling step carried out in advance.

The so prepared electrodes were used to assemble 2-electrode and 3-electrode lithium-ion half cells. A glass fiber separator was soaked with $LiPF_6$ (1M) in EC:DMC (1:1 molar ratio); it served as ion-conductor between the working electrodes and the counter electrode (Li metal). For the 3-electrode cells an additional Li-reference electrode was installed. Galvanostatic cycling with potential limitation combined with EIS was carried out with a Biologic potentiostat (VMP3) at room temperature; frequencies ranged from 1 mHz to 1 MHz. The 3-electrode Li-ion half cells were placed in a 1/2-inch T-tube fitting from Swagelok. The 2-electrode half cells were packed in a specially designed low-inductance electrochemical cell, which consists of an electrically insulating plastic without metallic springs and screws.

3. Results

To investigate the influence of the SEI to the electrical impedance response of a lithium ion half cell, two different anode materials were selected: graphite and $Li_4Ti_5O_{12}$ (LTO). While graphite is well known for its SEI growing properties during battery aging LTO is famous to be a long-life intercalation material [12–19]. In contrast to graphite, no, or at least negligible, SEI films are formed at LTO surfaces as it shows a relatively high operating potential (1.55 V) against Li metal [11].

For the aging measurement 3-electrode cells with working electrodes of graphite and $Li_4Ti_5O_{12}$ were assembled as described in section 2. During the cycling process several impedance spectra (shown in Fig. 1 using the complex plane plot, that is, the Nyquist representation) were recorded at different states of aging. In a Nyquist plot the imaginary part ($-Z''$) of the complex impedance $\widetilde{Z}$ is plotted vs the real part (Z').

While the fresh graphite cell features a high initial capacity than the one made with LTO, its reversible capacity plunges within a low number of charge-discharge cycles. On the other hand, the LTO structure, although starting at a lower reversible capacity level, seems to remain stable over more than 1000 cycles and hardly loses any capacity. This is usually related to the formation of significant passivation films on graphite that continue to grow and evolve in time. In contrast, LTO, which unlike graphite is a zero-strain material, forms virtually no SEI. Although some passivating films were reported on LTO, they were ascribed mostly to oxidation products diffusing from the positive electrodes [20].

Fig. 1 shows the impedance spectra recorded for the charged and discharged electrodes during cycle aging. In both cases inductive loops appear – independent of the anode material used and the aging status of the cell. To have final certainty about the influence