

On eliminating electrochemical impedance signal noise using Li metal in a non-aqueous electrolyte for Li ion secondary batteries

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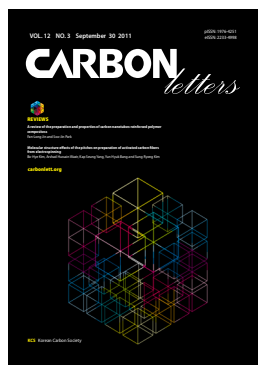
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Abstract

Li metal is accepted as a good counter electrode for electrochemical impedance spectroscopy (EIS) as the active material in Li-ion and Li-ion polymer batteries. We examined the existence of signal noise from a Li-metal counter quantitatively as a preliminary study. We suggest an electrochemical cell with one switchable electrode to obtain the exact impedance signal of active materials. To verify the effectiveness of the switchable electrode, EIS measurements of the solid electrolyte interphase (SEI) before severe Li⁺ intercalation to SFG6 graphite (at > ca. 0.25 V vs. Li/Li⁺) were taken. As a result, the EIS spectra without the signal of Li metal were obtained and analyzed successfully for the following parameters i) Li⁺ conduction in the electrolyte, ii) the geometric resistance and constant phase element of the electrode (insensitive to the voltage), iii) the interfacial behavior of the SEI related to the Li⁺ transfer and residence throughout the near-surface (sensitive to voltage), and iv) the term reflecting the differential limiting capacitance of Li⁺ in the graphite lattice.

Key words: electrochemical impedance spectroscopy, non-aqueous electrolyte, Li ion secondary batteries

1. Introduction

Electrochemical impedance spectroscopy (EIS) is an important tool in the field of chemistry, including electrochemistry, biochemistry and interfacial science. In particular, EIS is essential for revealing electrochemical phenomena such as the conducting behavior of polymer electrolytes, the interfacial behavior of the solid electrolyte interphase (SEI) on the electrode during the initial charge, and the characteristics of active materials with respect to repeated cycling [1-15]. However, careless handling of the electrode and cell components can cause significantly different EIS spectra for Li-ion secondary batteries [8-12]. Noticeable EIS noise of the active materials used in Li secondary batteries can arise when the counter electrodes are not appropriate. A good counter electrode should remain unchanged or inactive throughout an experiment because impedance signals from counter electrodes are fundamentally included in the measured results. In fact, it has been suggested that Li metal is very sensitive to an organic electrolyte and the sensitive SEI when it arises on its surface, especially showing an explicit EIS spectra divided into semi-circles and lines [5,8,9]. Li metal does not appear to be feasible for use as a counter electrode, though it has been accepted as the best choice for a counter electrode in half-cells for use in material development. The problem with Li metal is that it gives unpredictable signals with respect to the conditions, including the potential and type of surface film used. Along this line, the intent of this study is to check the electrochemical signal noise from Li metal quantitatively and then to remove the noise from a Li counter electrode by introducing an alternative counter electrode.

The key challenge for noise removal in this study is to introduce the same electrode as the working electrode as a half-cell. SEI formation on graphitic carbon before severe Li^+ intercalation was also investigated to show the advantages of doing this.

2. Experimental

For these experiments, Timrex SFG6 synthetic graphite (Timcal, Switzerland) was selected as the electrode material for Li intercalation behavior. It delivered an initial capacity of ca. 360 mAh g^{-1} and a high degree of graphitization, an expressed as $L_c > 100 \text{ nm}$ with a $(d_{002})_{\text{avg}}$ value of ca. 0.3355 nm . In the EIS experiment, we used the cell configurations shown in Fig. 1. The second and third electrodes from the left in Figs. 1a and b are identical. The third electrode was designated as the switchable one, acting as a working electrode in the case of Fig. 1a and then did as a counter electrode in the case of Fig. 1b. To elucidate whether Li metal is feasible as a counter electrode, several experiments were conducted.

3. Results and Discussion

Fig. 2 shows the EIS spectra with respect to the cell configurations labeled as A, B, C, D, E and F, as described in detail in Fig. 2. Two of these schemes (A, B) are not different except for the counter electrodes (C_1 in the case of A and Li in the case of B). B showed an additional depressed semi-circle compared to A. This type of semi-circle was likely due to SEI arising on the Li metal [4,8,9]. C_2 was discharged against the Li counter electrode (the fourth electrode from the left in Fig. 1a) to 0.8 V vs. Li/Li^+ and then stored immediately for 24 h at 25°C . Additional experiments were conducted using C_1 (Schemes C and D) and C_2 (schemes E and F) as the working electrode, respectively.

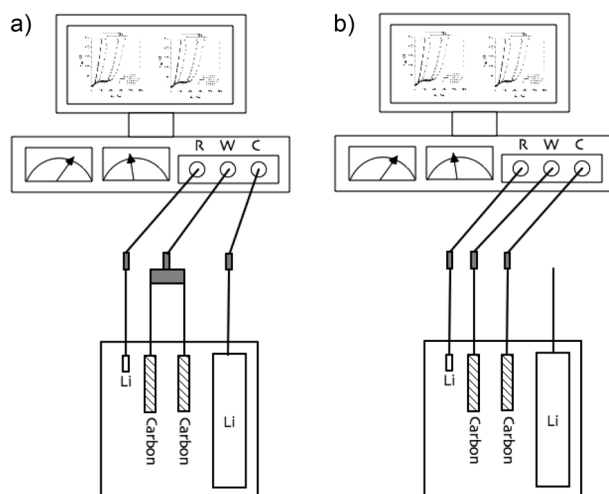


Fig. 1. Electrochemical cell-connection schemes: (a) cell connection for adjusting the potentials, (b) cell connection for measuring the impedances. R denotes the reference, W indicates working and C indicates counter. The carbon electrode weighs 10 mg and is $50 \mu\text{m}$ thick. $100 \mu\text{m}$ -thick Li foil was used for a reference chip electrode and for the counter electrode of (a).

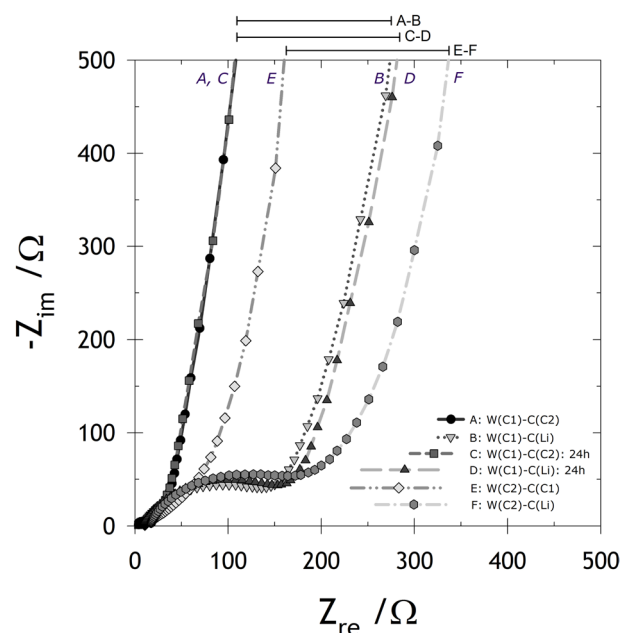


Fig. 2. Electrochemical impedance spectroscopy (EIS) spectra with respect to the cell configuration, C_1 : fresh SFG6, C_2 : initially fresh SFG6 after which it was adjusted at 0.8 V with Li : Li metal. Alternating current (AC) amplitude of 5 mV was the AC impulse at each potential during the EIS measurements.

In these cases, semi-circles in B, D and F were observed, serving as direct evidence of the incorporation of the signal from the counter electrode. The graphitic electrode has its impedance signal expressed as a semi-circle, which also indicates SEI on the electrode, if the semi-circles of the working carbon ($W(C_1)$ and $W(C_2)$) and the Li counter electrodes ($C(\text{Li})$) are coupled and if it is difficult and even impossible to decouple the signal of the counter electrode from the total EIS signal. Scheme D may also apply for a typically coupled EIS spectrum consisting of two semi-circles originating from both working and counter electrodes. In this study, we suggest that an electrochemical cell with one switchable electrode can be used to obtain the EIS spectra while eliminated the Li counter noise. This design consists of the SFG6 working electrode, the switchable SFG6 electrode, and two Li electrodes, as described at Fig. 1. This design avoids cell disassembly because the surface of the working electrode in the disassembled cell can be changed easily. As shown in Fig. 1, the SFG6 working electrode and the switchable SFG6 electrode were short-circuited by means of an outer metallic line while the specific potential was adjusted (Fig. 1a). After the removal of the outer metallic line shortly after the voltage adjustment, they were finally used as the working and counter electrodes, respectively, for the EIS measurement (Fig. 1b). The working and switchable SFG6 electrodes delivered equivalent electrochemical conditions, including the electrode potentials, in all experiment times.

To check the feasibility of using an electrochemical cell with the switchable SFG6 electrode, the electrochemical behavior of graphitic carbon during initial intercalation was investigated considering the electrochemical characteristics of the SEI that had formed in earlier studies [8,10,11,14,15]. Fig. 3 shows the

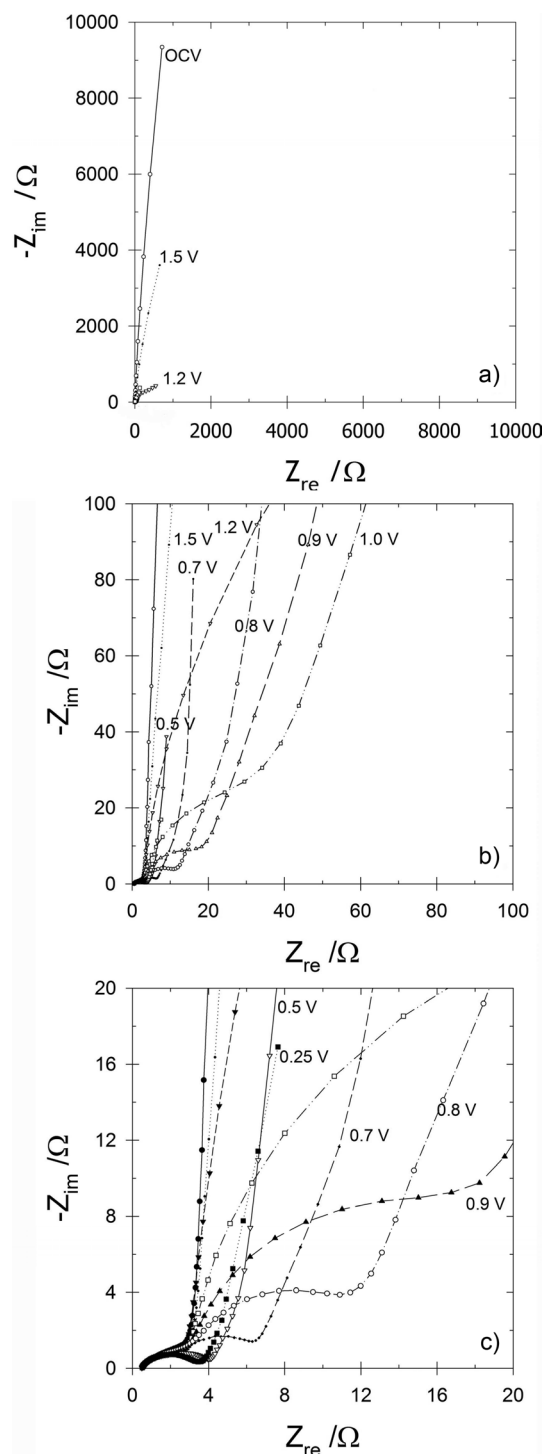


Fig. 3. Nyquist plots for synthetic graphite (SFG6) measured at the open circuit voltage (OCV) up to 0.25 V before severe Li^+ intercalation: (a) OCV-1.2 V, (b) 1.5-0.5 V, (c) 0.9-0.25 V. Note that a potential-sensitive semi-circle in the mid-frequency starts to appear at the potential of 1.2 V and converges from a potential of less than 0.5 V.

EIS spectra measured at from the open circuit voltage (OCV, ca. 3 V vs. Li/Li^+) to 0.25 V and Fig. 4 shows equivalent circuit models at >1.2 V and at <1.2 V. The notations on each element

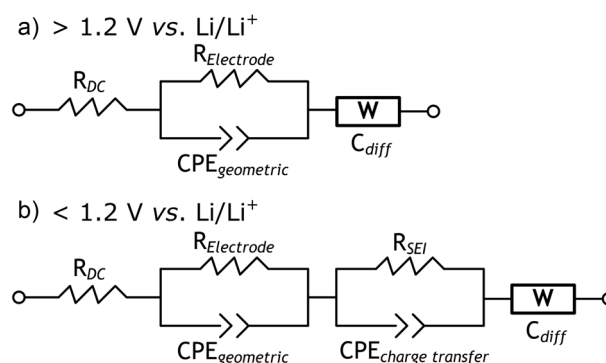


Fig. 4. Equivalent circuit models of SFG6 (graphitic material) a) >1.2 V, b) <1.2 V vs. Li/Li^+ , where R_{DC} is independent of the potential: $R_{Electrode}$ - $CPE_{geometric}$ changed slightly, but the behavior of R_{SEI} - $CPE_{charge transfer}$ showed a dramatic change with respect to the potential. The W element was inversely proportional to the differential limiting capacitance. CPE: constant phase element.

are defined in the caption of Fig. 4. The selected potential points for obtaining the EIS spectra were the OCV, 1.5, 1.2, 1.0, 0.9, 0.8, 0.7, 0.5 and 0.25 V. The EIS spectra of the graphitic carbon in Fig. 3c can be categorized simply as i) direct current (DC) resistance, ii) a potential-insensitive semi-circle in the high-frequency realm, iii) a potential-sensitive converged semi-circle, denoting the region in the mid-frequency realm, and iv) a linear region in the low-frequency realm. The DC resistance showed the same value in all of the selected potentials, reflecting the conductivity of the electrolyte used (1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$). The semi-circle in the high-frequency realm was observed even at the OCV and was insensitive to all selected potentials. There was no Li^+ population in or transfer into the carbon at the OCV. This likely represents geometric capacitance (a sort of constant phase element) and physical resistance depending on the physical structure of the electrode. Regarding the potential-sensitive semi-circle in the mid-frequency realm, it changed consistently with respect to the potential. Another capacitive-like element started to appear slightly at ca. 1.2 V and then clearly at ca. 0.5 V, where the newly formed semicircular region most likely indicated Li^+ residence and transfer in the SEI generated in this potential region. It should be noted that the semi-circle in the mid-frequency realm at 0.5-1.2 V was quite different from that of scheme C with the Li counter electrode, as shown in Fig. 2, which originated from another instance of SEI on the Li metal. This has been reported frequently in the case of Li working electrodes [8,14,15]. This potential-sensitive semi-circle in the mid-frequency realm can provide important information regarding the behavior of Li^+ transfer through and during the SEI. When formulating Li^+ transfer and residence through SEI with respect to the potential, resistance against Li^+ intercalation was lowered until its values were similar to those at a potential of less than 0.5 V. Because the SEI showed both capacitive and resistive behavior, as shown in Fig. 3c, if describing SEI geometrically, the semi-circle type of signal from the SEI can be conceived of as an interfacial region, including a slightly exfoliated surface. The line appeared in the low-frequency realm (Fig. 3a) likely indicates Li^+ finite length diffusion throughout the graphitic lattice; the end point of the line was found to be proportional inversely

to the differential limiting capacitance (C_{diff}) [8]. This line is very similar to those obtained using a specially prepared counter Li electrode [8,14,15].

4. Conclusions

EIS spectra with only the information of the working electrode material could be acquired using an electrochemical cell with an additional switchable electrode upon an energy-related material investigation. Based on our results, we note that Li metal is not feasible as a counter electrode when searching for an active material for Li secondary batteries. A switchable electrode equivalent to the working electrode is proposed as an alternative to a Li-metal electrode. If this is tested, data never previously obtained can be acquired, and this data will provide new information about energy storage materials such as Li ion batteries and electrochemical capacitors.

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References

- [1] Croce F, Nobili F, Deptula A, Lada W, Tossici R, D'Epifanio A, Scrosati B, Marassi R. An electrochemical impedance spectroscopic study of the transport properties of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$. *Electrochem Commun*, **1**, 605 (1999). [http://dx.doi.org/10.1016/s1388-2481\(99\)00123-x](http://dx.doi.org/10.1016/s1388-2481(99)00123-x).
- [2] Springer TE, Zawodzinski TA, Wilson MS, Gottesfeld S. Characterization of polymer electrolyte fuel cells using AC impedance spectroscopy. *J Electrochem Soc*, **143**, 587 (1996). <http://dx.doi.org/10.1149/1.1836485>.
- [3] Scrosati B, Croce F, Persi L. Impedance spectroscopy study of PEO-based nanocomposite polymer electrolytes. *J Electrochem Soc*, **147**, 1718 (2000). <http://dx.doi.org/10.1149/1.1393423>.
- [4] Peled E. The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems--the solid electrolyte interphase model. *J Electrochem Soc*, **126**, 2047 (1979). <http://dx.doi.org/10.1149/1.2128859>.
- [5] Belharouak I, Johnson C, Amine K. Synthesis and electrochemical analysis of vapor-deposited carbon-coated LiFePO_4 . *Electrochem Commun*, **7**, 983 (2005). <http://dx.doi.org/10.1016/j.elecom.2005.06.019>.
- [6] Belharouak I, Amine K. $\text{Li}_2\text{MTi}_6\text{O}_{14}$ (M=Sr, Ba): new anodes for lithium-ion batteries. *Electrochem Commun*, **5**, 435 (2003). [http://dx.doi.org/10.1016/s1388-2481\(03\)00090-0](http://dx.doi.org/10.1016/s1388-2481(03)00090-0).
- [7] Nagasubramanian G. Two- and three-electrode impedance studies on 18650 Li-ion cells. *J Power Sources*, **87**, 226 (2000). [http://dx.doi.org/10.1016/s0378-7753\(99\)00469-3](http://dx.doi.org/10.1016/s0378-7753(99)00469-3).
- [8] Aurbach D, Zaban A, Schechter A, Ein-Eli Y, Zinigrad E, Markovsky B. The study of electrolyte solutions based on ethylene and diethyl carbonates for rechargeable Li batteries. *J Electrochem Soc*, **142**, 2873 (1995). <http://dx.doi.org/10.1149/1.2048658>.
- [9] Kanamura K, Tamura H, Shiraishi S, Takehara ZI. XPS analysis of lithium surfaces following immersion in various solvents containing LiBF_4 . *J Electrochem Soc*, **142**, 340 (1995). <http://dx.doi.org/10.1149/1.2044000>.
- [10] Umeda M, Dokko K, Fujita Y, Mohamedi M, Uchida I, Selman JR. Electrochemical impedance study of Li-ion insertion into mesocarbon microbead single particle electrode. Part I. Graphitized carbon. *Electrochim Acta*, **47**, 885 (2001). [http://dx.doi.org/10.1016/s0013-4686\(01\)00799-x](http://dx.doi.org/10.1016/s0013-4686(01)00799-x).
- [11] Dokko K, Fujita Y, Mohamedi M, Umeda M, Uchida I, Selman JR. Electrochemical impedance study of Li-ion insertion into mesocarbon microbead single particle electrode. Part II. Disordered carbon. *Electrochim Acta*, **47**, 933 (2001). [http://dx.doi.org/10.1016/s0013-4686\(01\)00809-x](http://dx.doi.org/10.1016/s0013-4686(01)00809-x).
- [12] Dokko K, Mohamedi M, Umeda M, Uchida I. Kinetic study of Li-ion extraction and insertion at LiMn_2O_4 single particle electrodes using potential step and impedance methods. *J Electrochem Soc*, **150**, A425 (2003). <http://dx.doi.org/10.1149/1.1556596>.
- [13] Park CW. Li^+ storage characteristics in non-graphitizable carbons prepared from methylnaphthalene-derived isotropic pitch and graphitizable carbons prepared from needle cokes [PhD Thesis], Seoul National University, Seoul, Korea (2000).
- [14] Levi MD, Aurbach D. Diffusion coefficients of lithium ions during intercalation into graphite derived from the simultaneous measurements and modeling of electrochemical impedance and potentiostatic intermittent titration characteristics of thin graphite electrodes. *J Phys Chem B*, **101**, 4641 (1997). <http://dx.doi.org/10.1021/jp9701911>.
- [15] Levi MD, Aurbach D. Frumkin intercalation isotherm--a tool for the description of lithium insertion into host materials: a review. *Electrochim Acta*, **45**, 167 (1999). [http://dx.doi.org/10.1016/s0013-4686\(99\)00202-9](http://dx.doi.org/10.1016/s0013-4686(99)00202-9).