

In-Depth Investigation on Two- and Three-Electrode Impedance Measurements in Terms of the Effect of the Counter Electrode

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Although the three-electrode electrochemical cell is considered to be a powerful cell configuration for electrochemical impedance measurements, many researchers have extensively used the two-electrode electrochemical cell for the sake of convenience. In this work, the impedance of the lithium metal counter electrode that is frequently used to explore the electrochemical properties of the working electrode containing active materials in the field of lithium batteries was measured on the basis of a three-electrode electrochemical cell, and its contribution to the full cell impedance was carefully investigated. In particular, the effect of the counter electrode on the full cell impedance was quantitatively analyzed in the cases of cell aging and a low cell temperature. From the experimental results, it was demonstrated that inappropriate conclusions might be drawn in the case where a two-electrode electrochemical cell configuration is used to explore the impedance behavior of the active materials.

Keywords: electrochemical impedance spectroscopy, two-electrode impedance measurement, three-electrode impedance measurement, counter electrode

1. INTRODUCTION

Apart from its use as an anode material in primary lithium batteries, rechargeable lithium polymer batteries, *etc.*, lithium metal has been used as a counter or auxiliary electrode in the two- and three-electrode electrochemical cell configurations employed to characterize the electrochemical properties of the working electrode containing active materials.^[1] Resistance (or impedance) is considered to be one of the key parameters reflecting the cell performance because it causes the polarization of cells in operation and has a critical effect on the cell power and capacity. In order to evaluate the impedance properties of the active materials, electrochemical impedance spectroscopy (EIS) has been widely used. EIS provides information on the impedances of elementary reactions with different time constants, making possible the fundamental and systematic study of the electrode reactions and cell aging mechanism.^[2]

The three-electrode electrochemical cell configuration is basically used and recommended for investigating the impedance properties of the working electrode containing active materials. Nevertheless, many researchers have extensively used the two-electrode electrochemical cell, *e.g.*, a

two-electrode-based coin-type cell, to analyze the impedance properties of the working electrode on the assumption that the electrochemical activity of lithium metal is extremely high compared to that of the active materials of interest and, hence, the effect of the impedance of lithium metal on the full cell impedance is negligible.^[3-6]

However, the analysis of the electrochemical properties of active materials based on two-electrode impedance measurements could lead to incorrect conclusions unless the effect of the lithium metal counter electrode on the full cell impedance is fully understood. In this work, an in-depth investigation was conducted on the effect of the counter electrode on the full cell impedance measured in a two-electrode electrochemical cell configuration. For this purpose, a three-electrode electrochemical cell was constructed to differentiate the impedances of the working electrode containing the active materials and lithium metal counter electrode. Then, the resulting impedance of the working electrode was quantitatively compared with the full cell impedance obtained in the two-electrode impedance measurements in order to examine possible inconsistencies between the apparent impedance behaviors measured under the two- and three-electrode cell configurations. The impedance behaviors after cell aging and at a low cell temperature in these two sets of measurements were particularly focused on, and the discrepancies between them was critically discussed in terms of the

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effect of the lithium metal counter electrode.

2. EXPERIMENTAL PROCEDURE

Composite materials (working electrode) consisting of 90 wt.% LiCoO₂ (Aldrich), 5 wt.% carbon black, and 5 wt.% polyvinylidene fluoride (PVdF) binder in n-methyl pyrrolidone (NMP) were first pasted on the Al foil and then subsequently dried and pressed in the same manner as that described in our previous article.^[7] The mass of the active materials and the thickness of the composites were in the ranges of 15 mg to 25 mg and 65 mm to 75 mm, respectively. Lithium foil was used for the counter (or auxiliary) electrode. For the reference electrode, lithium titanate (Li₄Ti₅O₁₂)-PVdF composite was coated on a bare copper wire. Lithium titanate is considered an excellent alternative to lithium metal for the reference electrode in the Li-based redox system because its potential against the applied current has proved to be as stable as that of lithium. At the same time, it can be handled in normal atmosphere (air), which enables the reference electrode to be prepared with high reliability.^[8,9] Celgard 2400 was used for the separator and the electrolyte was a 1 M solution of lithium hexafluorophosphate (LiPF₆) in a 1:1 volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

Figure 1 shows the cell configuration used for the impedance measurements. The full cell impedance was measured during the two-electrode impedance experiments by taking ① and ③ in Fig. 1 as the counter/reference and working electrodes, respectively, while the impedance of the lithium metal counter electrode (or working electrode containing active materials) was obtained during the three-electrode impedance experiments by selecting ③ (or ①), ②, and ① (or ③) as the counter, reference, and working electrodes, respectively. All of the cells used for the experiments were assembled in a glove box (MBraun, Germany) filled with purified argon gas.

Before the experiments, the state of charge (SOC) of the lithium titanate reference electrode was set to *ca.* 50%, and,

in this state, the reference electrode shows a plateau potential of approximately 1.5 V (*vs.* Li/Li⁺). For the analysis of the impedance behavior in the course of cell aging, first, the as-prepared cell was cycled five times between 3.0 V and 4.1 V (*vs.* Li/Li⁺) at a rate of 0.2 C (the cell in this state is called the “fresh cell” hereafter). Then, the full cell impedance and the impedances of the lithium metal counter electrode and working electrode containing LiCoO₂ active materials were measured under two- and three-electrode cell configurations, as explained in Fig. 1. After the impedance measurements, the cell was further cycled ten times at a rate of 0.5 C (the cell in this state is called the “aged cell” hereafter). The capacity retention of the “aged cell” was *ca.* 91% of that of the “fresh cell”. Finally, the full cell, counter electrode, and working electrode impedances of the “aged cell” were obtained in the same manner as that for the “fresh cell”. In the case of the impedance tests at low cell temperatures, the full cell, counter electrode, and working electrode impedances of the “fresh cell” were measured at temperatures of 20°C, -10°C, and -20°C.^[10,11] All of the impedance tests were performed at a cell potential of 4.1 V (*vs.* Li/Li⁺) over the frequency range of 100 kHz to 5 mHz. A Solartron 1287 electrochemical interface was used for the galvanostatic charge/discharge cycling, and it was coupled with a Solartron 1455A frequency response analyzer for the electrochemical impedance measurements.

3. RESULTS AND DISCUSSION

In order to ensure the reliability of the three-electrode impedance measurements adopted in this work, the full cell impedance and counter/working electrode impedances of the “fresh cell” were obtained at ambient temperature. As shown in Fig. 2(b), the *calculated full cell impedance* determined by the summation of the impedance spectra of the working and counter electrodes (Fig. 2(a)) proved to have quantitative coincidence with the experimental full cell impedance measured in the two-electrode cell configuration, indicating that our impedance tests are self-consistent: the absolute values

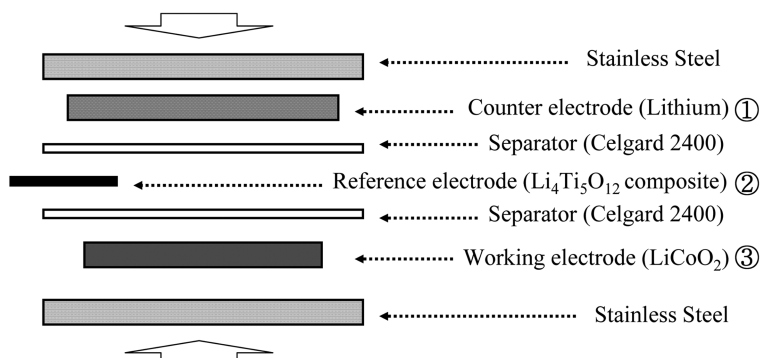


Fig. 1. Schematic illustration of the electrochemical cell used for the impedance measurements.

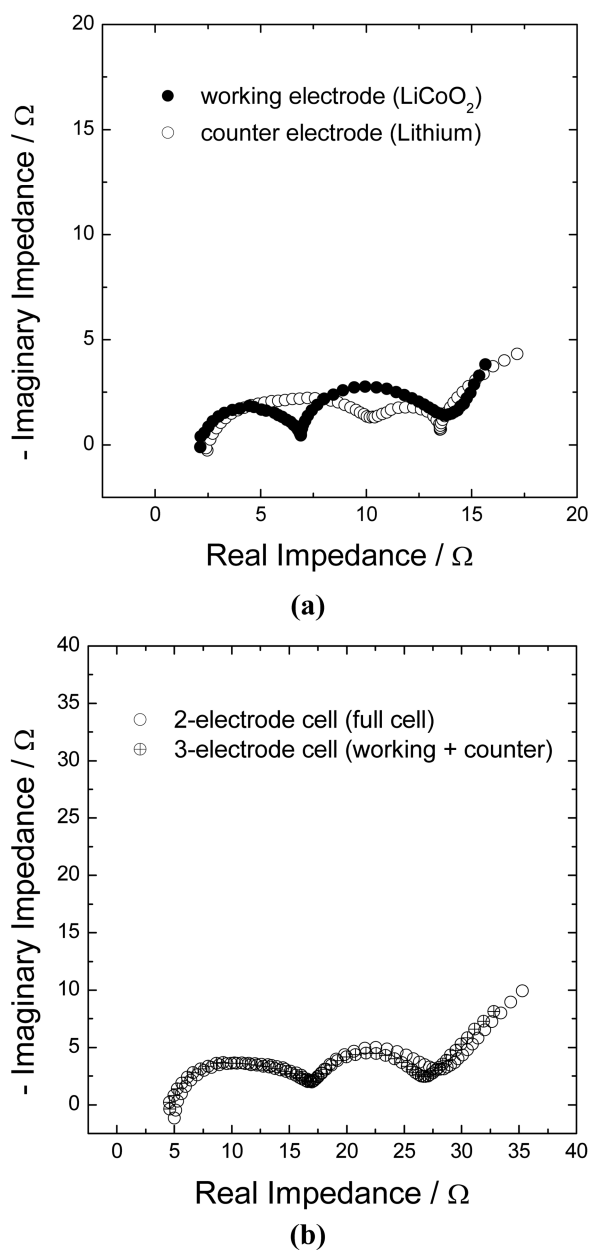


Fig. 2. (a) Impedance spectra of the working electrode containing active materials (solid circle) and the lithium metal counter electrode (open circle) obtained from the fresh cell at a cell potential of 4.1 V (vs. Li/Li⁺). (b) Impedance spectra measured under two-electrode electrochemical cell configuration (open circle) and the summation of the impedance spectra of working and counter electrodes (crossed circle).

of the calculated and experimental impedances obtained from the test cells revealed a relatively small discrepancy of less than 10%. This implies that the impedance spectra determined by the two- and three-electrode measurements in this work are quite reliable.

Next, three different “fresh cells” with the same cell chemistry and configuration were prepared to roughly inspect the

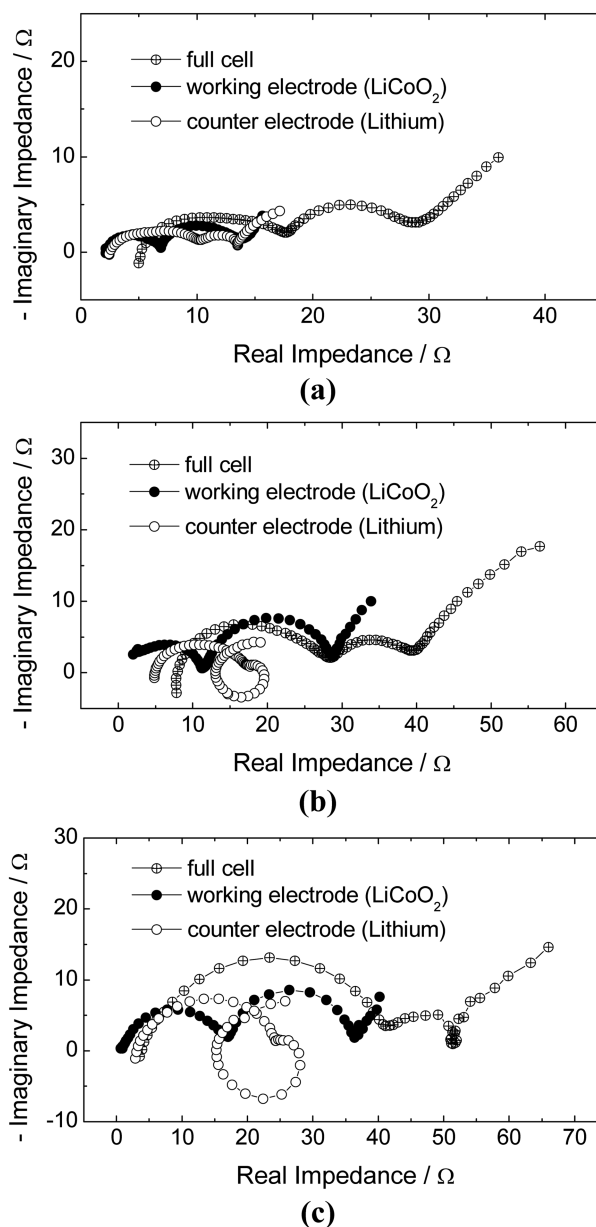


Fig. 3. Typical impedance spectra of full cell, working electrode, and counter electrode at a cell potential of 4.1 V (vs. Li/Li⁺).

effect of the lithium metal counter electrode on the full cell impedance. The impedances of lithium metals are characterized by an inductive loop in the intermediate frequency range, albeit with different sizes (Fig. 3). It has been reported that the intermediate-frequency inductive loop can be ascribed to the disturbance of the specific electrochemical reactions by *e.g.* the absorbates.^[12,13] Nevertheless, as far as we know, the origin of the inductive behavior of lithium metal has yet to be clarified.

On the other hand, it is worthwhile noting that the real impedances of the lithium metal counter electrode are comparable in value to those of the working electrode containing

the active materials, *i.e.*, the contribution of lithium metal to the full cell impedance reaches *ca.* 30% to 50%, as shown in Fig. 3. As a matter of fact, the impedance of the working electrode is quite sensitive to the design parameters, such as the surface/geometrical properties of the active materials, loading of active materials on the substrate, composition/density of the electrode composite, *etc.* This means that the relative contribution of the lithium metal counter electrode to the full cell impedance is dependent on the design parameters of the working electrode. Nevertheless, the results in Fig. 3 tell us that the effect of lithium metal on the full cell impedance is quite considerable and should not be neglected for the proper understanding of the impedance spectra obtained from the two-electrode cell configuration. That is to say, the impedance of lithium metal critically influences the value and shape of the full cell impedance. This further indicates that two-electrode impedance measurements adopting lithium metal as a counter electrode might not be an appropriate test method to characterize the impedance properties of the working electrode containing active materials.

For an in-depth investigation of the effect of the lithium metal counter electrode on the full cell impedance during the two-electrode impedance measurement, the relative contribution of lithium metal was systematically studied in two exemplary cases of cell aging and low cell temperature, both of which result in an increase in the full cell impedance. A comparative analysis was made between the full cell impedance (in the two-electrode impedance measurement) and the impedance of the working electrode (in the three-electrode impedance measurement), and, on this basis, it is suggested that the analysis of the full cell impedance might lead to improper conclusions being drawn with regard to the electrochemical properties of the active materials if the effect of the lithium metal counter electrode is ignored.

3.1. Impedance Behavior during Cell Aging

Figs. 4(a), (b), and (c) show the impedances of the full cell, working electrode containing active materials (LiCoO_2), and lithium metal counter electrode, respectively, for the “fresh cells” (solid circles) and the “aged cells” (open circles) at a cell potential of 4.1 V (*vs.* Li/Li^+). Although both the full cell impedance (Fig. 4(a)) and impedance of the working electrode (Fig. 4(b)) consist of two semi-circles (arcs) and an inclined line, there were remarkable differences in the size of the arcs, slope of inclined lines, and the degree of change in the arc size (*i.e.*, resistance) after cell aging. In order to determine whether the differences can be totally ascribed to the contribution of the counter electrode, as mentioned above, a more quantitative analysis of the impedance spectra is necessary.

For this purpose, the total cell reactions and the reactions in the working electrode were modeled based on the full cell and working electrode impedances, respectively, as follows:

first of all, since the two arcs and inclined line in the full cell impedance (Fig. 4(a)) included the impedance of the lithium metal counter electrode, it is quite unlikely that these impedance signals have some physical meaning. Therefore, the arcs were phenomenologically modeled by a parallel arrangement consisting of a resistance R and a dispersed capacitance CPE (constant phase element), while the inclined line was electrically expressed as the apparent Warburg impedance, $Z_{W,app}$, because it seems to have a similar shape to the Warburg impedance (Z_W). On the other hand, it is generally agreed that the first arc in the impedance spectra of the working electrode (Fig. 4(b)) is caused by the parallel combination of the resistance to Li^+ ion transport through the solid electrolyte interphase (SEI), R_f , and the dispersed SEI capacitance, CPE_f , or the combination of the particle-to-particle contact resistance, R_{con} , and the dispersed contact capacitance, CPE_{con} .^[14,15] Also, the second arc is attributed to the parallel arrangement of the interfacial charge transfer resistance, R_{ct} , and the dispersed double layer capacitance, CPE_{dl} . Finally, the inclined line is modeled by the Warburg impedance, Z_W , due to the solid-state lithium diffusion in the active materials.^[16]

The resulting equivalent circuits constructed for the full cell and working electrode containing active materials are shown in the insets of Figs. 4(a) and (b), respectively. All of the electrical parameters and the diffusion coefficient of lithium were determined by using the complex non-linear least squares (CNLS) fittings, and the results are summarized in Table 1 and Fig. 5.

When we take a closer look at the changes in the resistances measured in the two-electrode electrochemical cell before and after cell aging, it is noted that the resistance R_2 from the second arc of Fig. 4(a) increased by about 10 Ω after cell aging, which corresponds to a *ca.* 105% increase compared to that of the “fresh cell”, whereas the resistance R_1 from the first arc and the apparent Warburg coefficient $A_{W,app}$ remained relatively unchanged. If we try to estimate, from these results, the change in the elementary impedances of the active materials on the assumption that the impedance behavior measured in the two-electrode electrochemical cell configuration is identical to that of the working electrode containing active materials, we might conclude that R_2 is the only resistance that is affected in the course of cell aging.

However, the impedance behavior of the working electrode, obtained from the three-electrode electrochemical cell configuration, was found to be quite different from the above expectation. As shown in Table 1, the resistance R_f (or R_{con}) from the first arc of Fig. 4(b) was increased by 43.7 % after cell aging, while the resistance R_{ct} from the second arc was elevated by 45.6 %. That is, the quantitative contributions of R_f (or R_{con}) and R_{ct} to the total increase in impedance of the “aged cell” were almost equivalent. This indicates that the strategy employed to stabilize the impedance of the active

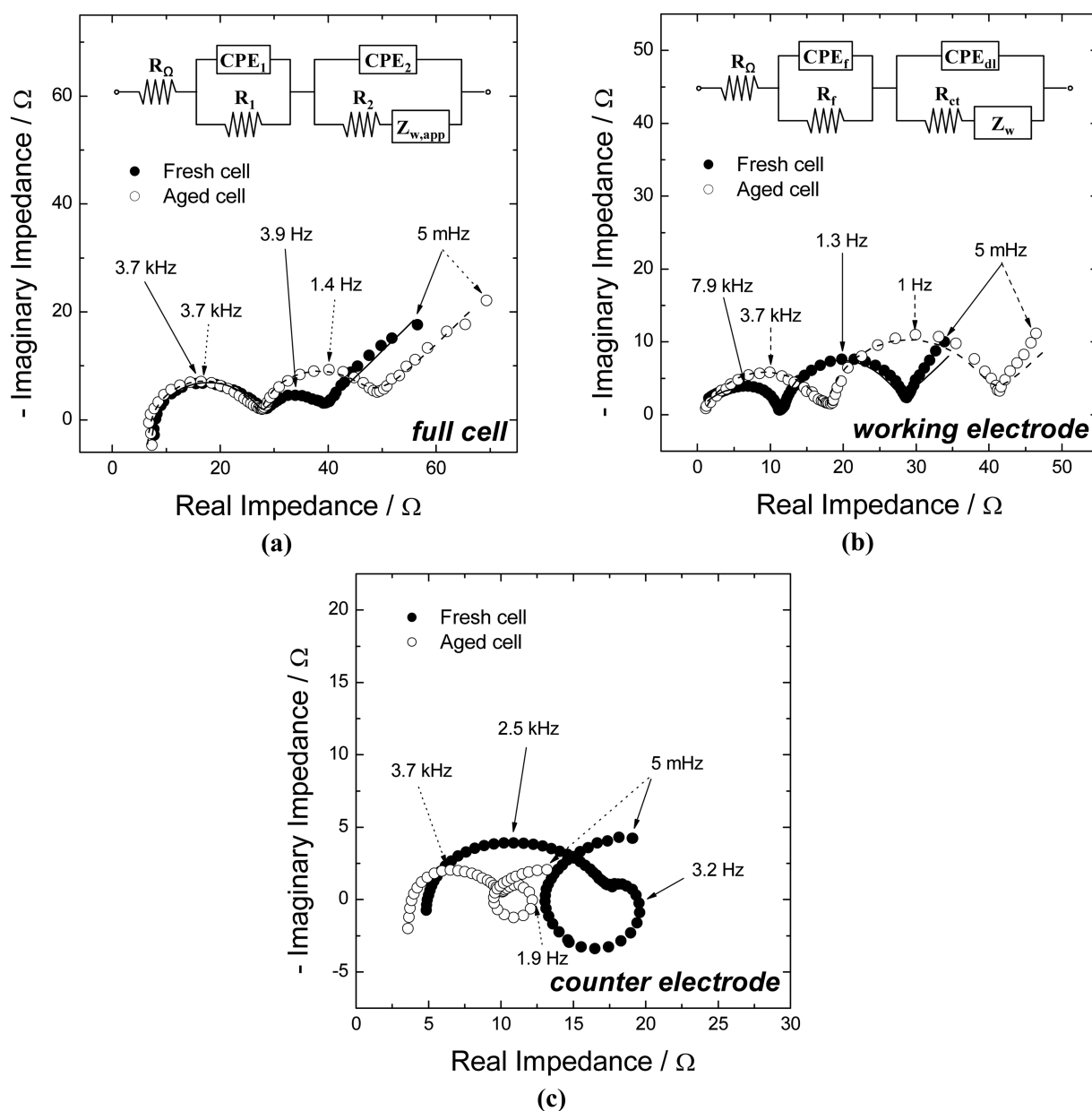


Fig. 4. Impedance spectra of (a) the full cell, (b) working electrode, and (c) counter electrode, obtained from the fresh (solid circle) and the aged cell (open circle) at a cell potential of 4.1 V (vs. Li/Li⁺). The insets on (a) and (b) are the equivalent circuits to roughly model the overall battery reactions and the reactions in the working electrode, respectively. Solid and dashed lines were determined from the CNLS fittings of the impedance spectra to the equivalent circuits.

materials has to include the design of the cell components to suppress the increase both in the interfacial charge transfer resistance and Li⁺ ion transport resistance through the SEI (or particle-to-particle contact resistance).

The origin of the difference in the elementary impedances and their changes with cell aging between the full cell impedance (measured in the two-electrode electrochemical cell) and the impedance of the working electrode (measured in the three-electrode electrochemical cell) is fairly straightforward when we consider the impedance behavior of the

lithium metal counter electrode (Fig. 4(c)) before and after cell aging: the sizes of the high-frequency arc and the intermediate-frequency inductive loop of the impedance spectra of the lithium metal in the “fresh cell” were relatively large, in terms of their absolute values compared to those in the “aged cell”. When the high-frequency arc of lithium metal was added to the impedance signal of the working electrode, the increase in the first arc of the working electrode in the “aged cell” diminished, making the size of the first arc of the full cell impedance nearly invariable before and after cell

Table 1. Electrical parameters of (a) the full cell and (b) working electrode containing active materials at different aging levels, determined from the complex non-linear least squares (CNLS) fittings of the impedance spectra to the equivalent circuits.

(a)								
	R_1 (Ω)	$CPE_1^{(1)}$		R_2 (Ω)	$CPE_2^{(1)}$		$A_w^{(2)}$ ($\Omega \cdot s^{-0.5}$)	$D^{(3)}$ ($\times 10^{-13} m^2 \cdot s^{-1}$)
		C ($\mu F \cdot s^{\eta-1}$)	η		C ($mF \cdot s^{\eta-1}$)	η		
Fresh cell	21.6	29.8	0.74	9.4	4.6	0.89	4.62	0.63
Aged cell	21.7	22.5	0.76	19.3	4.8	0.92	5.37	0.46
(b)								
	R_f (Ω)	$CPE_f^{(1)}$		R_{ct} (Ω)	$CPE_{dl}^{(1)}$		$A_w^{(2)}$ ($\Omega \cdot s^{-0.5}$)	$D^{(3)}$ ($\times 10^{-13} m^2 \cdot s^{-1}$)
		C ($\mu F \cdot s^{\eta-1}$)	η		C ($mF \cdot s^{\eta-1}$)	η		
Fresh cell	11.9	36.6	0.69	14.7	7.6	0.99	1.98	3.41
Aged cell	17.1	25.6	0.76	21.4	6.6	0.96	2.29	2.55

⁽¹⁾Constant phase element (CPE) was expressed in the form of $C(j\omega)^{\eta}$

⁽²⁾ A_w is the Warburg coefficient.

⁽³⁾ D at 4.1V (vs. Li/Li⁺) was estimated from the ac technique.^[21,22]

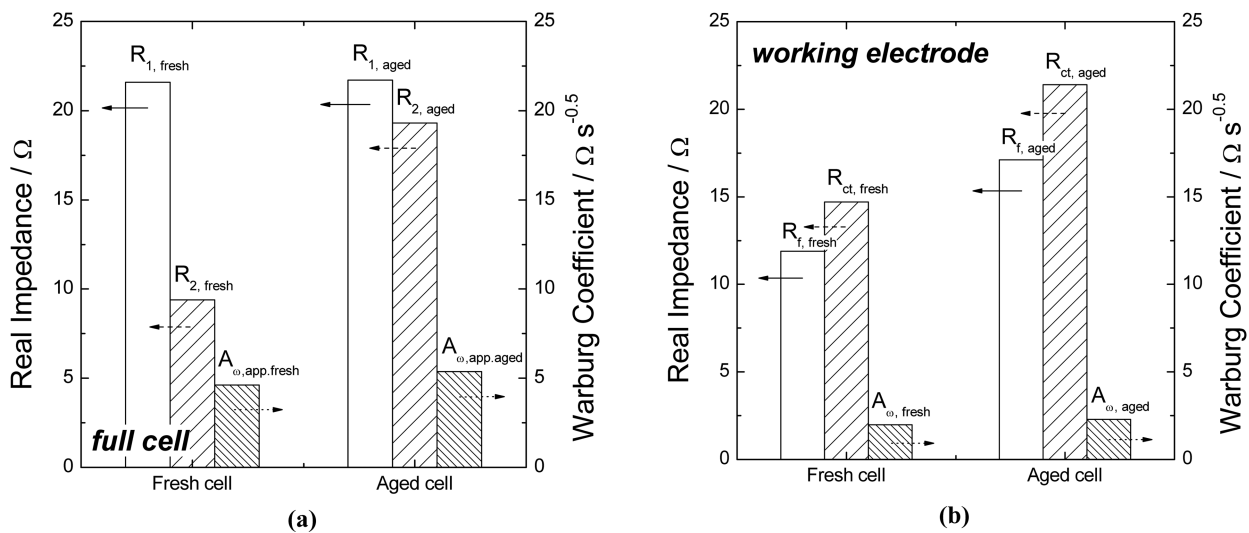


Fig. 5. Changes in individual real impedances and (apparent) Warburg coefficient with cell aging (a) in the full cell and (b) in the working electrode.

aging. On the contrary, the second arc of the full cell impedance became larger after cell aging compared to that of the working electrode due, undoubtedly, to the decrease in the size of the intermediate-frequency inductive loop of lithium metal. That is to say, the impedance of the lithium metal counter electrode has substantial influence on the full cell impedance in the course of cell aging and results in a significant discrepancy in the arc sizes in the high and intermediate frequency ranges between the full cell impedance and the impedance of the working electrode.

In regards to the Warburg impedance in the low frequency range, the following two points are noteworthy. The first one is the disagreement between the Warburg coefficients A_w or diffusion coefficients, calculated from the low-frequency

inclined lines in the full cell impedance and the impedance of the working electrode (see Table 1 and Fig. 5). The highest frequencies of the inclined line of the impedance spectra in Figs. 4(a) and (b) were estimated to be 0.4 Hz and 0.06 Hz, respectively, indicating that the apparent Warburg impedance $Z_{w,app}$ (Fig. 4(a)) has a smaller time constant than the real Warburg impedance Z_w (Fig. 4(b)). This disagreement is caused by the distortion of the Warburg tail of the working electrode by the low-frequency signal of the lithium metal counter electrode (Fig. 4(c)). This inevitably leads to a difference in the lithium diffusion coefficient that is calculated on the basis of the Warburg impedance.^[17,18] The diffusion coefficient determined from Fig. 4(a) was *ca.* 5.4 times smaller than that obtained from Fig. 4(b), as shown in Table 1.

This strongly indicates that the diffusion coefficient of lithium could be underestimated if we use the full cell impedance for its calculation instead of the impedance of the working electrode.

The second noteworthy point is the slope of the Warburg impedance. The Warburg impedance Z_W of the working electrode (Fig. 4(b)) showed a higher slope (about 55°) than that which would be expected for ideal solid-state diffusion (*i.e.*, 45°). The positive deviation of the Warburg slope is ascribed to the dispersed time constant for diffusion or the distribution of the diffusion length (due to *e.g.* the geometrical irregularity of the active materials).^[19-22] On the other hand, it appears that the slope of the apparent Warburg impedance $Z_{W,app}$ of the two-electrode cell (Fig. 4(a)) corresponds to the ideal slope of 45° . It is quite clear that this 45° -inclined line originated from the decrease in the phase angle of the low-frequency impedance spectra of the lithium metal counter electrode with decreasing frequency (Fig. 4(c)) and is far from the ideal diffusion process in bulk materials.

3.2. Impedance Behavior at Low Cell Temperatures

A number of studies reported that such battery performance characteristics as capacity and power are critically decreased at low cell temperature and suggested that the abrupt increase in the cell impedance or polarization with decreasing temperature might be the main reason for this, based on the results obtained from two-electrode impedance measurements.^[3-5] Therefore, it would be quite interesting to determine how much the impedance of the lithium metal counter electrode affects the full cell impedance at different cell temperatures.

Figure 6(a) shows the impedance spectra of the full cell at cell temperatures of -10°C and -20°C , measured under the two-electrode electrochemical cell configuration. Comparing the ambient-temperature impedance spectra (solid line in the figure), two points of difference are noteworthy. One is the absence of an inclined line (*i.e.*, Warburg impedance) in the low-temperature impedance spectra, which results from the increase in the time constant with decreasing cell temperature. The other important point is that the ambient-temperature impedance spectra consist of two arcs while the low-temperature impedance spectra appear to have three distinct arcs (see the magnification in Fig. 6). The presence of three arcs means that at least three different parallel combinations of resistor and capacitor are involved in the total battery reaction. It is reasonable to suggest that the transition from two-arc to three-arc behavior is due to the low-temperature differentiation of two processes whose RC time constants are very close to each other at ambient temperature, which is generally observed when there is a substantial difference in the activation energies of the two processes. The three-arc behavior can be simply modeled by a series connection of three *R-C* (or *R-CPE*) parallel elements, as presented in the

inset of Fig. 6. On the other hand, considering that the typical impedance spectra of LiCoO_2 show two-arc behavior, the three arcs observed in the full cell impedance at low temperature are difficult to understand on the basis of the electrode reaction of the working electrode.

Figures 6(b) and (c) show the impedances of the working electrode containing active materials (LiCoO_2) and a lithium metal counter electrode, respectively, at ambient and low cell temperatures, measured under the three-electrode electrochemical cell configuration. Unlike the impedance spectra of the full cell, the impedance spectra of the working electrode are composed of two arcs, irrespective of the cell temperature. It is particularly noteworthy that the elementary impedances (or arcs) of the lithium metal counter electrode increased significantly with decreasing cell temperature. A closer look at the frequency ranges in which the individual arcs emerged on the impedance spectra of the working (Fig. 6(b)) and counter electrodes (Fig. 6(c)) proves that the three arcs in the full cell impedance spectra are attributable to the combination of the arcs in the impedance spectra of the working and counter electrodes.

For the quantitative analysis, all of the electrical parameters of the equivalent circuits suggested in Figs. 6(a) and (b) were determined by CNLS fittings, and the results are summarized in Table 2 and Fig. 7. The temperature dependences of the three arcs in the full cell impedance had no relationship with those of the two arcs in the working electrode impedance. That is, the low-temperature impedance of the full cell is quite different in shape and value from that of the working electrode containing active materials due, primarily, to the effect of the lithium metal counter electrode. Accordingly, the full cell impedance determined by the two-electrode impedance measurement cannot provide any useful information on the impedance properties of the active materials in the working electrode.

4. CONCLUSIONS

In the present work, the impedances determined in two- and three-electrode electrochemical cell configurations were carefully analyzed in terms of the effect of the lithium metal counter electrode. The results are summarized as follows:

1. The impedances of the lithium metal counter electrode were characterized by an inductive loop in the intermediate frequency range, and the real impedance of lithium metal was found to be comparable in value to that of the working electrode containing active materials (LiCoO_2). This indicates that the impedance of lithium metal critically affects the value and shape of the full cell impedance and, hence, the two-electrode impedance measurement adopting lithium metal as a counter electrode is not a reliable method of investigating the impedance properties of the active materials.
2. There was a remarkable increase in the second arc in the

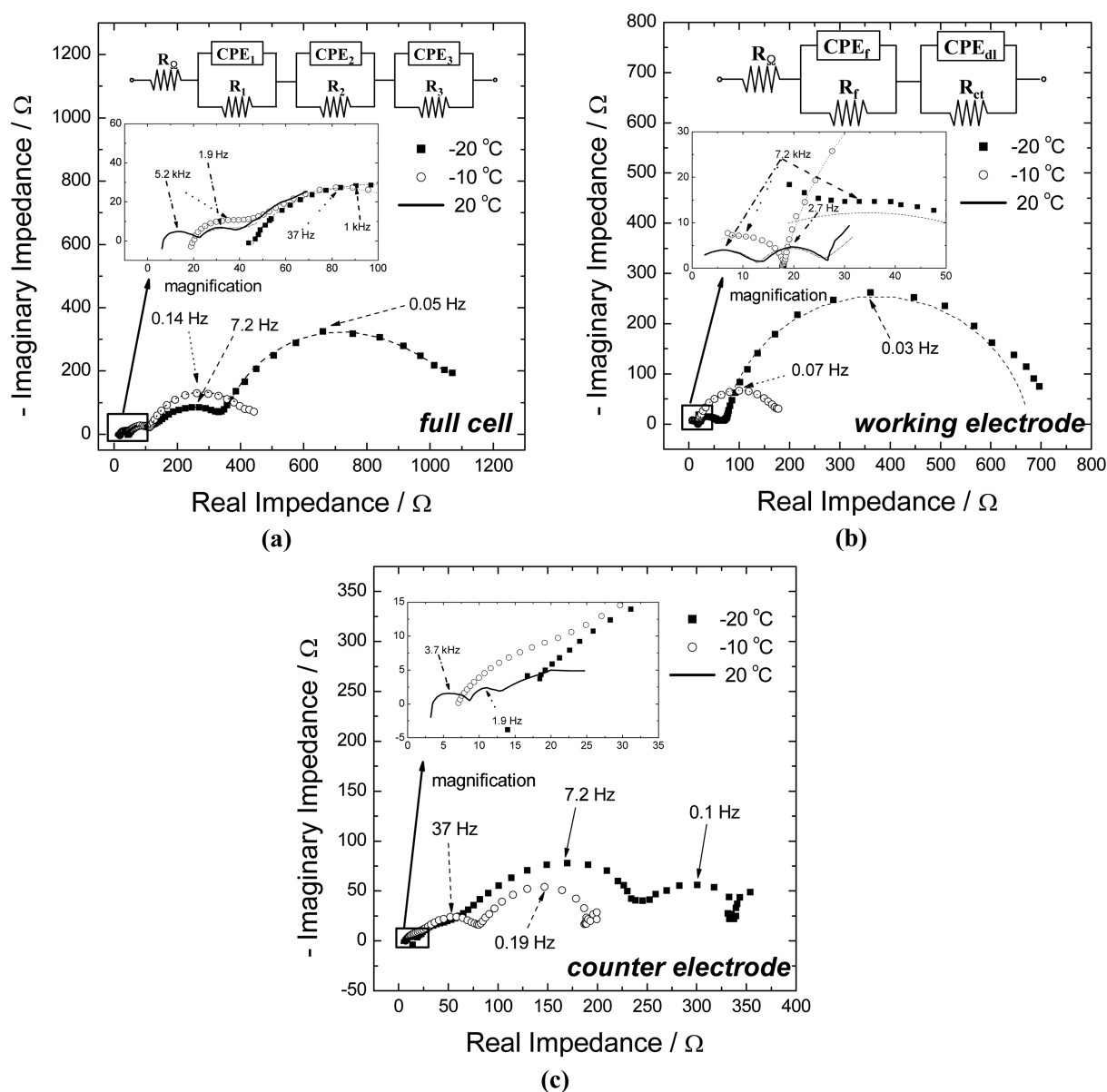


Fig. 6. Impedance spectra of (a) the full cell, (b) working electrode, and (c) counter electrode at a cell potential of 4.1 V (vs. Li/Li⁺) and cell temperatures of 20 (solid line), -10 (open circle), and -20 °C (solid square). The insets on (a) and (b) are the equivalent circuits to roughly model the overall battery reactions and the reactions in working electrode, respectively. Dashed lines were determined from the CNLS fittings of the impedance spectra to the equivalent circuit.

full cell impedance spectra of the “aged cell” compared to the corresponding arc of the “fresh cell”, while the first arc and the apparent Warburg coefficient remained relatively unchanged. On the contrary, both the first and second arcs in the impedance spectra of the working electrode were considerably increased after cell aging, greatly contributing to the full cell impedance. At the same time, the lithium diffusion coefficient was underestimated when the full cell impedance, instead of the impedance of the working electrode, was used for its calculation and the positive deviation of the Warburg slope in the impedance spectra of the working electrode

was apparently concealed by the signal of the lithium metal counter electrode.

3. The low-temperature impedance spectra of the full cell showed three-arc behavior, while the impedance spectra of the working electrode were composed of two arcs, irrespective of the cell temperature. This proved that the three arcs in the full cell impedance spectra are attributable to the combination of the arcs in the impedance spectra of the working and counter electrodes. From the quantitative analyses, it is concluded that the temperature dependences of the three arcs in the full cell impedance had no relationship with those of

Table 2. Electrical parameters of (a) the full cell and (b) working electrode containing active materials at different cell temperatures, determined from the complex non-linear least squares (CNLS) fittings of the impedance spectra to the equivalent circuits.

(a)									
Temp. (°C)	R ₁ (Ω)	CPE ₁		R ₂ (Ω)	CPE ₂		R ₃ (Ω)	CPE ₃	
		C (μF · s ^{η-1})	η		C (mF · s ^{η-1})	η		C (mF · s ^{η-1})	η
20	15.7	29.9	0.74	5.1	~0.01	1	22.4	11.5	0.62
-10	30.7	21.1	0.71	67.2	0.2	0.80	300	3.9	0.89
-20	87.9	29.1	0.65	226	0.2	0.77	669	4.6	0.94

(b)							
Temp. (°C)	R _f (Ω)	CPE _f		R _{ct} (Ω)	CPE _{dl}		
		C (μF · s ^{η-1})	η		C (μF · s ^{η-1})	η	
20	11.4	8.1	0.79	13.0	38	0.70	
-10	17.4	12.8	0.86	165	0.4	0.95	
-20	62.8	6.5	0.85	633	16	0.58	

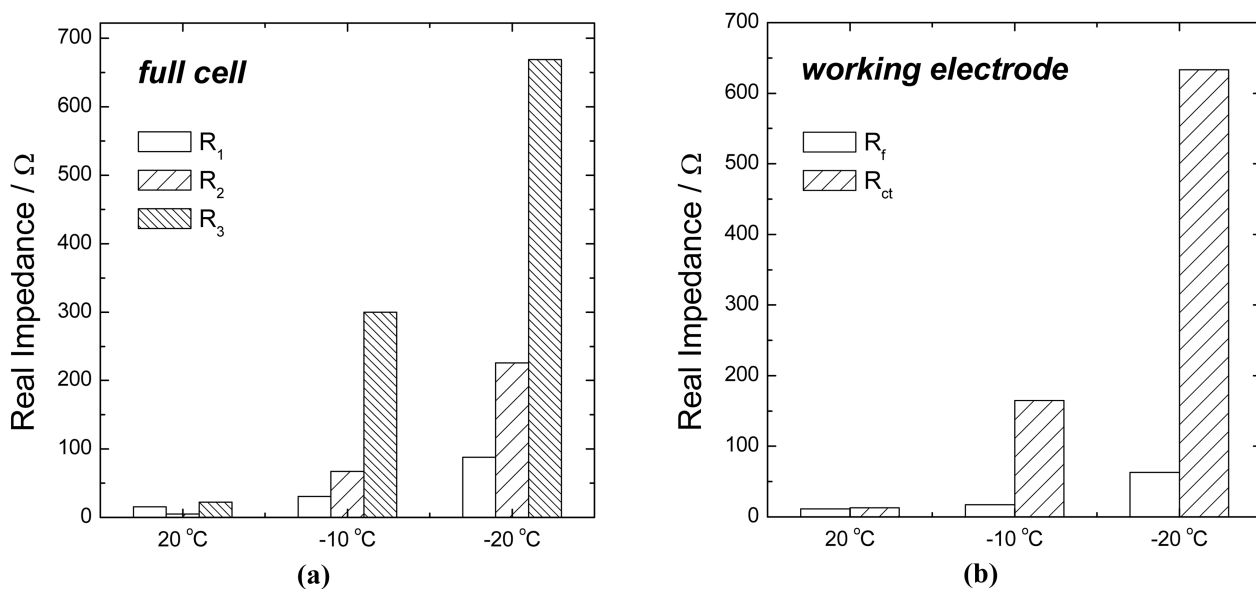


Fig. 7. Changes in individual real impedances with cell temperature (a) in the full cell and (b) in the working electrode.

the two arcs in the working electrode impedance due, primarily, to the strong effect of the lithium metal counter electrode.

4. In the cases of both cell aging and low cell temperature, the impedance of the lithium metal counter electrode has substantial influence on the value and shape of the full cell impedance over the whole frequency range, resulting in a significant discrepancy in the impedance behaviors between the full cell and working electrode. This strongly indicates that the two-electrode electrochemical cell configuration adopting lithium metal as a counter electrode is not reliable to characterize the impedance properties of the working electrode containing active materials, and, hence, much caution should be taken regarding the effect of the lithium metal

counter electrode when analyzing the full cell impedance spectra obtained under a two-electrode cell configuration, such as a typical coin-type cell.

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