Area-specific Impedance of a Single Lithium Insertion Electrode: A Measure to Evaluate Polarization

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Lithium insertion materials are usually examined in lithium cells and the rechargeable capacities together with potential profiles are specifically obtained and evaluated in terms of energy density. Polarization measurements of lithium insertion electrodes are very difficult to perform in a usual manner, so that rate-capability tests of the lithium cells have been done substituting for polarization measurements. Something associated with polarization is missing in describing basic research results on lithium insertion materials. In this paper, a method to measure area-specific impedance of a single lithium insertion electrode is presented, by which the polarization of a single lithium insertion electrode can be evaluated.

If the area-specific impedance of a single electrode is known, cell impedance of lithium-ion battery is calculated and then polarization, i.e., voltage response, for any input or output current is also calculated by a Fourier transform method [1]. Therefore, the area-specific impedance of a single lithium insertion electrode is a measure to evaluate polarization. The problem is how to measure the area-specific impedance of a single lithium insertion electrode.

Zero-volt lithium-ion cells with a symmetric parallel-plate electrode configuration (SPEC) have been applied to the big voltage polarization measurements [2] and the determination of the rate of side reaction on a lithium insertion electrode [3]. In order to measure the area-specific impedance of a single lithium insertion electrode, the same method is applied. Figure 1 shows the charge and discharge curves of the zero-volt lithium-ion cell of lithium titanium oxide (LTO; $Li[Li_{1/3}Ti_{5/3}]O_4$). Because the cell is 0 V, the terms of charge and discharge have no meaning. “Charge” means the increase in voltage and “discharge” decrease in this paper. As can be seen in Fig. 1, the cell works well around 0 V. Figure 2 shows the results on the impedance measurements of the zero-volt lithium-ion cell. The cell consists of two identical LTO-electrodes separated by two-sheets of polypropylene non-woven cloth 30μm thick in which the electrolyte is absorbed. Consequently, the area-specific impedance of an LTO-electrode in ohm cm^2 is obtained by dividing the absolute value of the cell impedance by 2 and multiplying by 2. The active electrode area does not affect the phase angle in Fig. 2 due to the complex impedance. It should be noted that the area specific impedance reported here contains the impedance of the 30μm-thick separator together with the electrolyte at present. Trials on its separation are still under way.

As has been briefly described above, we report the area-specific impedance of single lithium insertion electrodes as a new measure to evaluate polarization of lithium insertion electrodes. Applications of the basic impedance data to battery design will be highlighted, through which internal resistance affecting input and output power is known in advance of making actual batteries.

References

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2. T. Ohzuku et al., *J. Solid State Electrochem*., **12**, 979 (2008).
3. K. Nakura, et al., *J. Electrochem. Soc*., **158**, A1243 (2011).

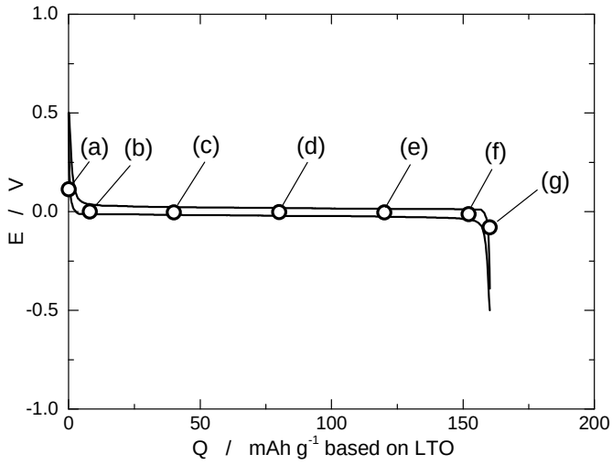

Fig. 1 Charge and discharge curves of a zero-volt lithium-ion cell of LTO operated in voltage ranging from –0.5 to +0.5 V at 0.25 mA cm^{-2} at room temperature for 5 cycles. The cell is discharged to (a) 0, (b) 5, (c) 25, (d) 50, (e) 75, (f) 95, and (g) 100% of the depth of discharge (DOD) and open-circuited, at which the impedance is measured. One electrode is 35.3 mg LTO-mix 124 μm thick and the other is 35.9 mg mix 124 μm thick. The electrolyte is 1 M $LiPF_6$ ethylene carbonate / dimethyl carbonate (3/7 by volume). The separator used is two-ply propylene nonwoven cloth 30 μm thick. The LTO-mix consists of 88wt% LTO, 6wt% acetylene black, and 6wt% PVdF. The active electrode area is 2 cm^2.

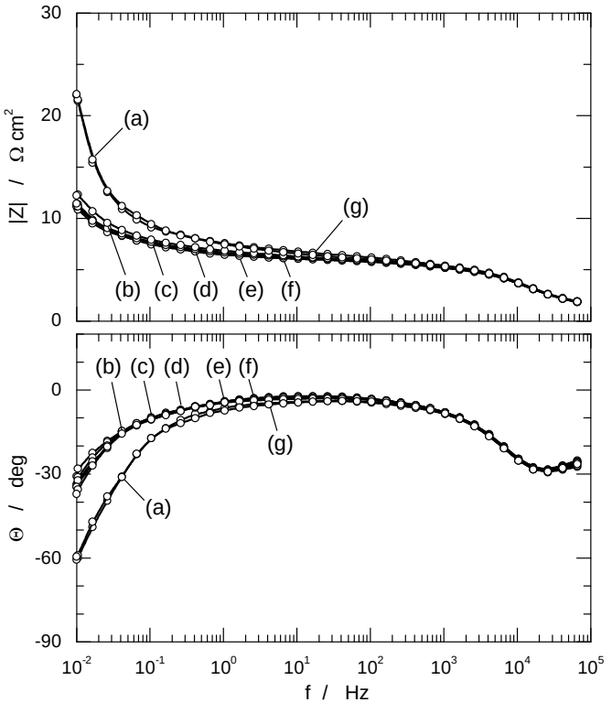

Fig. 2 The area-specific impedance of an LTO-electrode obtained by using a zero-volt lithium-ion cell with SPEC; (a) 0, (b) 5, (c) 25, (d) 50, (e) 75, (f) 95, and (g) 100% of DOD. The absolute value of the impedance is plotted in a linear scale, not a logarithmic scale. The area-specific impedance of an LTO-electrode is independent of the state of charge (SOC) except near 0 and 100% of SOC.