Two- and Three-electrode Impedance Spectroscopy Studies for Lithium-ion Batteries

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Objectives

Recently, there has been intensive research in lithium ion batteries due to their high energy and complex interface between electrolytes and electrodes. Impedance spectroscopy is one of the most promising tools for the modeling and diagnosis of interfacial reactions, for lithium ion batteries. Earlier researchers had proposed and analyzed that impedance in this system is resulted from many factors, such as charge transfer, Li^+ diffusion in electrodes, passive film etc. [1-4]. However, the shape and value of the resistance in impedance spectrum are strongly affected by solvents, particle sizes and thickness of electrodes, stack pressure etc. Without systematical and integrated comparison of these spectra, incorrect interpretations could arise. So we did systematical impedance studies with two-electrode and three-electrode systems and then analyze the variation of impedance during cycling test. Finally, we also applied this method to industrial batteries.

Results

Interfacial impedance between PVDF/HFP-based electrolytes and lithium metal, although still growing, could attain delicate kinetic equilibrium upon prolonged storage. Graphite, on the other hand, was found to remain inert toward PVDF/HFP membranes. Its interfacial impedance did not vary with increasing storage time or with different lithium salts. However, it was found that the lithium-side impedance of a Li/C half cell could often induce misleading information of the carbon electrode and thus a three-electrode impedance study was called for under this condition. We found, in particular, that an inductive loop would appear in the low-frequency region of the impedance spectrum of a carbon electrode right after the first lithium-intercalation step, probably implying that an adsorption/desorption phenomenon might exist at the interface. Moreover, another inductive effect arising from the connecting leads also appeared at high-frequency region. Finally, the positive electrode was found to be the major source of cell impedance and it increased with increasing cycle number.

Conclusions

1. The impedance of a carbon electrode reduces once after the first lithium-intercalation step. In parallel, an inductive loop would appear in the low-frequency region of the impedance spectrum, probably implying that an adsorption/desorption phenomenon might exist at the interface.
2. For the batteries with smaller interior resistance, inductive effect arising from the connecting leads would appear at high-frequency region.
3. The impedance spectrum of the two-electrode system is equal to the sum of spectra of the positive and negative electrode in a three-electrode system.
4. The major source of cell impedance is resulted from the positive electrode in a lithium-ion battery.

References

1. D. Aurbach, B. Markovsky, I. Weissman, E. Levi, and Y. Ein-Eli, *Electrochimica Acta*, **45**, 67-86 (1999).
2. E. Karden, S. Buller, and R. W. De Doncker, *J. Power Sources*, **85**, 72-78 (2000).
3. G. Nagasubramanian, *J. Power Sources*, **87**, 226-229 (2000).
4. Y. C. Chang and H. J. Sohn, *J. Elecrochem. Soc.*, **147 (1)**, 50-58 (2000).