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Applications of AC Impedance Spectroscopy as Characterization and Diagnostic Tool in Rechargeable Energy Storage Devices

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Electrochemical Impedance spectroscopy (EIS) is exceptionally powerful and rapidly evolving technique for investigating electrical properties of materials and electrochemical interfacial kinetic processes in wide variety of practical systems and applications. The method offers the most powerful on-line and off-line analysis of the status of investigated media, electrodes, and probes in many different complex time– and space-resolved processes that occur in electrochemical laboratory experiments or over a lifetime of monitored samples, devices, or materials. EIS is useful as an empirical quality control procedure that can also be employed to interpret fundamental electrochemical processes [1, 2].

At NASA Glenn Research Center the EIS technique is being widely and effectively employed in characterization and performance monitoring of rechargeable energy storage devices, such as states of electrodes during charging / discharging cycles in secondary batteries and fuel cells. The technical objective for batteries is to improve the performance of rechargeable lithium-ion cells to meet the energy storage requirements of human missions. The approach is to develop advanced battery components to safely provide substantially higher specific energy for relatively few charge/discharge cycles. Impedance spectroscopy has been widely applied to monitoring developed lithium-ion batteries, most prominently to the studies of Li^+ insertion / intercalation into active material on anodes and cathodes during the battery charging/discharging cycles. Applications of EIS method allowed for efficient *in* situ performance monitoring of various types of electrodes and electrolytes used in experimental Li-ion batteries, such as anodes based on traditional graphite and nanotechnology modified silicon-carbon composites; cathodes based on lithiated mixed-metal-oxide formulations of Ni-Mn-Co and Ni/Co/Al; and various modifications of organic carbonate-based flame-retardant electrolytes. The studies included evaluating performance of separate battery components in half-cells, as well as complete impedance analysis of full cells.

A choice of conductive solvent is based on a compromise between its conductivity over a wide temperature range and its ability to develop a passivating layer on the intercalating host surface. Anodes and cathodes are frequently being separately investigated by the EIS using a three-electrode configuration using Li-metal counter electrode and Li-metal reference electrodes. Charging and discharging studies are performed as a function of potential vs Li reference electrode, or as a function of Li+ content in the graphite anode material. The system on separately analyzed cathode and anode can usually be represented by equivalent circuit diagram. For a complete battery system, the impedances of all components must be added together.

At NASA Glenn Research Center No Flow through Proton exchange membrane fuel cells (NFT PEMFC) are being developed for variety of aerospace and land-based applications. The technical objective for NFT PEMFC is to increase the efficiency and reliability of the core technologies needed to create energy source with minimal mass and volume and required safety and operability. This system consists of a primary fuel cell, electrolyzer, and balance-of-plant components. The primary fuel cell creates electricity, water, and heat by the electrochemical conversion of hydrogen and oxygen. The electricity is used to drive a load, depleting the stored hydrogen and oxygen. These reactants are regenerated by the electrolyzer, which electrolyzes the product water using electricity generated from photovoltaic arrays. Balance-of-plant components such as transducers and valves manage all flows required for operation.

The conclusions about relative contributions of different segments of PEMFC to the measured impedance are achieved on the basis of changes in their responses to variations in drawn current density, temperature, membrane thickness, fuel composition (concentrations of hydrogen, oxygen, presence of CO), and humidity level. This approach frequently allows various sections of the impedance spectra to be assigned to cathode, anode, and electrolyte–related contributions. The EIS analysis of RPEMFC has been effectively utilized to identify and separate different ohmic, mass- and charge-transfer limiting processes. The impedance spectrum changes and EIS model can also be used as diagnostic tool to detect changes in levels of humidity, current density, catalyst poisoning, and other operational parameters. EIS also is capable of diagnosing several common causes of fuel cell failure, such as the membrane drying, flooding with water from the cathode reaction, and anode catalyst poisoning.

References

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2. M. Orazem, B. Tribollet, “Electrochemical Impedance Spectroscopy”, John Wiley & Sons, New York, 2008.