NMR STUDY OF LITHIUM INTERCALATION IN $Li_xV_2O_5$ ELECTRODES

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The important characteristics of a rechargeable lithium-ion battery are that the charging/discharging process should be nearly reversible, energy efficient, and have minimal physical changes. During charging/discharging, a number of phases and large changes in structure typically develop at the electrodes of battery cell. Some of the phases and structure changes are irreversible, thus resulting in capacity decay with cycles, low energy efficiency, and low cycle life.

In order to understand where and what kind of irreversible processes occur at the electrodes, and how do these processes affect the capacity, energy efficiency, and cycle life of the battery, high-resolution nuclear magnetic resonance (NMR) spectroscopic measurements and were involved to the identification of phases, structure changes, and the maximum ion uptake in the electrodes.

A battery test system was used to study the discharge capacities as a function of number of cycle for a Li(anode)/$Li_xV_2O_5$(cathode) buttery cell battery (as shown in Figure 1). It can be seen that the initial capacity of the battery was about 27 mAh, and the cycle lifetime of the battery was less than 20 cycles. ^{7}Li NMR spectra of $Li_xV_2O_5$ cathodes at different charge states were investigated. Different ^{7}Li NMR spectra were obtained from $Li_xV_2O_5$ cathodes from a fully charged, fully discharged, and dead cells, which were represented as samples (A), (B), and (C), respectively (as shown in Figure 2). Two resonance signals at chemical shifts of 0 and -20 ppm was found to be correspond to Li^+ from residual electrolyte and $Li_xV_2O_5$, respectively, were obtained. The variation of the ^{7}Li NMR spectra and the spin-lattice relaxation times (T_1) varied with different charge states and temperatures.

^{51}V NMR spectra show even more significant difference for $Li_xV_2O_5$ cathodes at different charge states (as shown in Figure 3). For fully charged $Li_xV_2O_5$ cathode with minimum concentration of Li-ion, the NMR spectrum with a broad chemical shift was obtained and was quite similar to the standard V_2O_5 single crystal sample. However, for fully discharged $Li_xV_2O_5$ cathode, the signal profile and intensity were very different due to the change of V ion from V^{+5} to V^{+4}.

AC impedance spectrometer was used to measure the impedance of Li/$Li_xV_2O_5$ cells at different charge states at 300 K (as shown in Figure 4). The semi circles at medium frequency, which corresponds to Li transport at the interface between the liquid electrolyte and the $Li_xV_2O_5$ electrode surface, were very different for cells at different charge states. AC impedance spectra were also measured at different temperatures. The correlation of the electrochemical properties and the NMR spectra will be discussed.

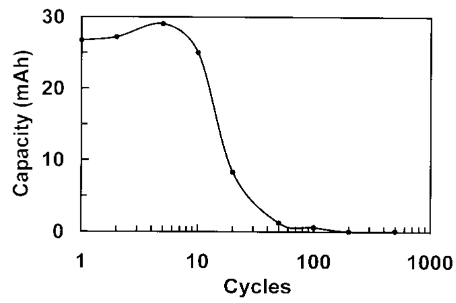

Figure 1 Capacities of the battery as a function of cycle numbers during discharge process.

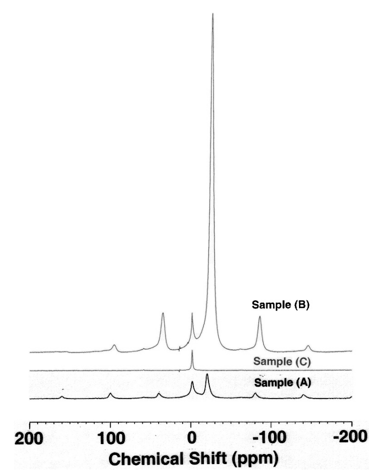

Figure 2 ^{7}Li NMR spectra of different $Li_xV_2O_5$ cathodes at temperature of 300 K and spin rate of 4 kHz.

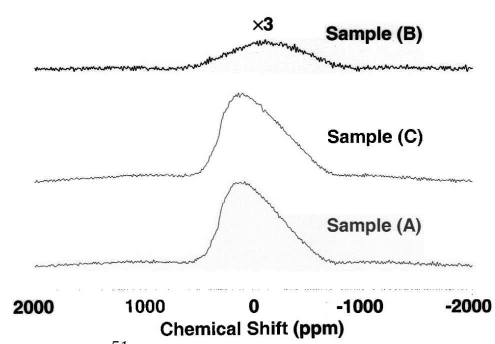

Figure 3 Static ^{51}V NMR spectra of different $Li_xV_2O_5$ cathodes at temperature of 300 K.

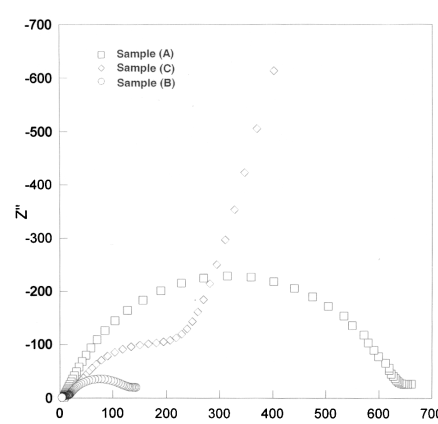

Figure 4 AC impedance spectra of Li/$Li_xV_2O_5$ cell at different charge states.