

## Investigation of Li-Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> Rechargeable Batteries at Different Charged States Using NMR Spectroscopy

Z. Ma<sup>(1),§</sup>, P. Moss<sup>(2)</sup>, R. Fu<sup>(1)</sup>, G. Au<sup>(3)</sup>, E.J. Plichta<sup>(3)</sup>, and J.P. Zheng<sup>(2),(4),\*</sup>

<sup>(1)</sup>Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310

<sup>(2)</sup>Department of Electrical and Computer Engineering, Florida A&M University and Florida State University, Tallahassee, FL 32310

<sup>(3)</sup>U.S. Army Communications-Electronics Command, Ft. Monmouth, NJ 07703

<sup>(4)</sup>Center for Advanced Power Systems, Florida State University

<sup>§</sup>Present address: Department of Chemistry, University of Utah, Salt Lake City, UT 84112

( Received May 31, 2003 ; received in revised form July 30, 2004 )

**Abstract:** Li rechargeable cells made with structural arrangement Li/membrane/ Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> were examined under three states using NMR spectroscopy; these states are charged, discharged, and over-cycled. <sup>7</sup>Li NMR signals at chemical shifts of 0 ppm and around -20 ppm from the resonance frequency, which corresponds to the Li ions from the residual electrolyte at the cathode surface and inside the cathode material of Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>, respectively, were obtained from Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> samples in both charged and discharged cells. From nuclear spin-lattice relaxation time (T<sub>1</sub>) measurements, two components due to the Li ions in the electrode surface region and inside the bulk of Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> particles were obtained from charged cell. The <sup>51</sup>V NMR spectra were virtually identical for Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> from the charged and over-cycled cells; however, the intensity of <sup>51</sup>V NMR signal from the discharged cell was significantly lower due to paramagnetic V<sup>+4</sup> and V<sup>+3</sup> species.

Key words : Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> cathode, <sup>7</sup>Li NMR, <sup>51</sup>V NMR

### 1. INTRODUCTION

Numerous techniques have been used to understand mechanisms of the degradation of Li rechargeable batteries. Most studies were performed using traditional electrochemical methods including charge/discharge cycling, and ac impedance spectroscopy to develop the relationship between the capacity degradation and the resistance increasing of the battery [1-7]. The nuclear magnetic resonance (NMR) was used to evaluate the immediate structural and electronic environment of Li and other ions in a variety of host materials for both crystalline and amorphous phases [8-10]. Many NMR studies have been focused on the anode materials to understand the effect of carbon structure and morphology on reversible Li capacity. It was demonstrated that very different NMR characteristics associated with Li den-

drates and intercalated Li in carbon used as anode electrode [11,12], and distinct portions such as due to the reversible and irreversible Li [12], or the covalently bond and metallic Li [13], appeared on <sup>7</sup>Li NMR spectra with different chemical shifts. For cathode electrodes, a small fraction of excess Li and impurities in LiCoO<sub>2</sub> could be detected from the feature and linewidth of <sup>7</sup>Li NMR spectra [14,15]. In this work, we have used NMR spectroscopic methods to probe the structure and electronic environment of Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> cathode electrodes from batteries, which were charged to three extreme charge states such as charged, discharged, and over-cycled states. The electronic environment of Li and V ions was characterized by using NMR spectroscopy.

### 2. EXPERIMENTAL

Panasonic<sup>®</sup> vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) lithium-rechargeable batteries were used as experimental samples. The button cell

\*To whom correspondence should be addressed: E-mail address: zheng@eng.fsu.edu

batteries were made with Li (anode)/separator/  $\text{Li}_x\text{V}_2\text{O}_5$  (cathode), and were rated at 30 mAh. A porous polymer membrane was used as a separator. The aluminum mesh and stainless steel bottom case of the button cell were used as the current collectors for anode and cathode electrodes, respectively. The cell has 23 mm in diameter and 2.0 mm in thickness.

An Arbin battery test system was used for charge and discharge cycling of cells. During the charge cycle, a constant voltage mode of 3.4 V was applied as all rechargeable Li-ion batteries used; and during discharge, a constant current mode at 10 mA was used in order to easier control the cell to be charged to different charged states.

Three different samples for NMR studies were prepared as follows: One cell (charged cell) was charged to 3.4 V at a constant voltage mode; one cell (discharged cell) was discharged to 2.1 V at a constant current (10 mA) mode; and one cell (over-cycled cell) was continuously charged and discharged until the cell had a capacity of almost zero. Then these cells were opened, the  $\text{Li}_x\text{V}_2\text{O}_5$  cathode electrode materials were removed from cells and packed into NMR rotors in a glove box filled with Ar gas for NMR studies.

The  $^7\text{Li}$  NMR measurements were performed on Bruker DMX-300 spectrometers with  $^7\text{Li}$  NMR frequency of 116.66 MHz using a 4 mm Bruker magic angle spinning (MAS) double-resonance NMR probe. An aqueous LiCl (1M) was used as an external chemical shift reference. The  $^7\text{Li}$  spin-lattice relaxation times ( $T_1$ ) were measured using an inversion recovery pulse sequence. The static  $^{51}\text{V}$  NMR measurements were performed on Bruker DRX-833 spectrometer with a  $^{51}\text{V}$  NMR frequency of 218.66 MHz using a home-built single resonance 4 mm MAS probe.

### 3. RESULTS AND DISCUSSION

The battery was cycled in a voltage range from 2.0 to 3.4 V. Figure 1 shows voltage-capacity curve during discharge process at 25 °C. Plateaus are observed as the voltage discharge from 3.4V to 2.0V and comparing these plateaus to the previous works [21-23], it has been determined that in this voltage discharge interval the  $\text{Li}_x\text{V}_2\text{O}_5$  structure undergoes at least three distinct phase changes,  $\alpha$ ,  $\delta$ , and  $\gamma$ . The charge and discharge capacities were calculated from the charge and discharge cycle. It was found that the initial capacity of the cell was about 35 mAh; however, after 26 cycles, the capacity reduced to less than 15% of the initial capacity [20]. From previous studies [21-23], the different phase was formed in  $\text{Li}_x\text{V}_2\text{O}_5$  with different  $x$ -value of Li insertion. When cell was charged to 3.4 V, the  $\text{Li}_x\text{V}_2\text{O}_5$  was  $\alpha$ -phase with Li concentration of  $0.1 < x < 0.2$ ; when the cell was discharged to 2.1 V, it was  $\gamma$ -phase with Li concentration of  $1.6 < x < 1.8$ .

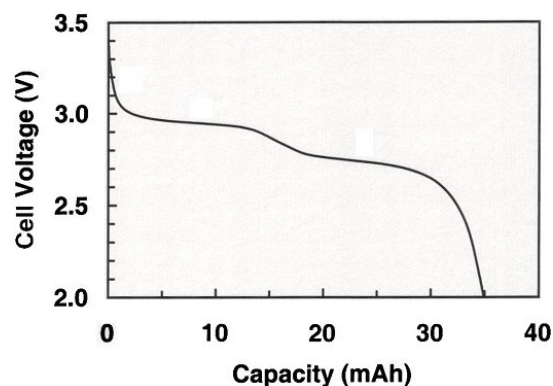


Figure 1: Voltage-capacity curve of Li/separators/ $\text{Li}_x\text{V}_2\text{O}_5$  cell during discharge process.

Figure 2 shows the static  $^7\text{Li}$  NMR spectra measured from a 300 MHz spectrometer for  $\text{Li}_x\text{V}_2\text{O}_5$  samples from cells with different charged states. For samples at charged and over-cycled states, a resonance signal at chemical shift of 0 ppm was obtained. The signal was assigned to the Li ions from the residual electrolyte, because it was found that the signal disappeared after the sample was washed in propylene carbonate (PC) solvent. Another signal with peak at around -20 ppm was obtained from charged cells. The signal at the low frequency was due to the Li ions in  $\text{Li}_x\text{V}_2\text{O}_5$  electrode. The width of the signal at 0 ppm was narrower compared to the signal at low frequencies; it indicated that the Li ion in the liquid electrolyte was more mobile than that in solid  $\text{Li}_x\text{V}_2\text{O}_5$  electrode material. From samples at discharged state, the resonance signal was dominated by a broad signal with peak also at 20 ppm; however, the magnitude and the width of the signal at 20 ppm from charged and discharged cells were very different, and they reflected directly the Li concentration in  $\text{Li}_x\text{V}_2\text{O}_5$  for different charge states. It can be seen that the Li concentration in  $\text{Li}_x\text{V}_2\text{O}_5$  from the discharged cell was much higher than that from the charged cell. It can also be seen that no Li signal was detected from the inside of  $\text{V}_2\text{O}_5$  electrode material from the over-cycled cell. From Figure 2, it can also be seen that the linewidth of  $^7\text{Li}$  NMR spectrum from a discharged cell was broader than that from a charged cell. It is because that for the charged cell, the Li concentration is low, the diamagnetic  $\text{V}^{+5}$  species in  $\text{Li}_x\text{V}_2\text{O}_5$  is dominated; however, for the discharged cell, Li concentration increases and both  $\text{V}^{+5}$  and  $\text{V}^{+4}$  species co-existed in  $\text{Li}_x\text{V}_2\text{O}_5$  due to the charge compensation. The interaction with the paramagnetic  $\text{V}^{+4}$  is the source of the large linewidths.

Figure 3 shows the  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}_x\text{V}_2\text{O}_5$  samples from different charged cells at spin rate of 7 kHz at 25 °C. Similarly to the spectra obtained at static state, two resonance signals were obtained. The signal at chemical shift of 0 was from Li ions in residual electrolyte. Another signal at chemi-

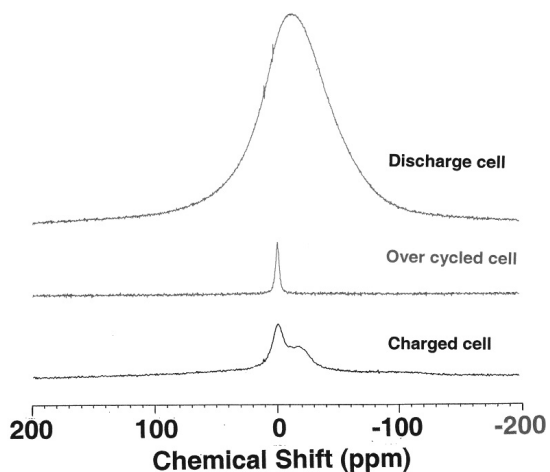


Figure 2: Static  $^7\text{Li}$  NMR spectra of  $\text{Li}_x\text{V}_2\text{O}_5$  cathodes at room temperature.

cal shift of -20 and -25 ppm was obtained for samples from the charged and discharged cells, respectively; however, for over-cycled cell, only signal from Li ions in residual electrolyte was obtained, and no side band signals were obtained, which means that Li ions in electrolyte are quite mobility, which is consistent with the observation from static NMR spectra as shown in Figure 2. Figure 4 shows the recovery of  $^7\text{Li}$  NMR signals recorded from  $\text{Li}_x\text{V}_2\text{O}_5$  samples from (a) the discharged and (b) charged cells. It was found that for discharged  $\text{Li}_x\text{V}_2\text{O}_5$  sample, the recovery could be described by a single-exponential component at  $T_1=333$  ms; however, for charged  $\text{Li}_x\text{V}_2\text{O}_5$  sample, the recovery process could be fitted by two-exponential components. The slow and fast components of  $T_1$  were 105 and 15 ms, respectively. The signal obtained from discharged sample and the slow component of charged sample are assigned to the contribution from Li ions inside bulk of  $\text{Li}_x\text{V}_2\text{O}_5$  particles. The  $T_1$  and chemical shift differences from two samples were caused by the different environmental factors of Li ions, including the Li ions concentration in charged sample is much lower than that in discharged sample and Li ions in charged sample is mostly surrounded by  $\text{V}^{+5}$  ions rather than by  $\text{V}^{+4}$  and  $\text{V}^{+3}$  ions in discharged sample. The fast component of 15 ms from charged sample is 7 times faster than the slow component and is possibly due to the contribution of Li ions in the electrode surface region. The reason that no fast component was obtained from discharge sample is because the Li ions in the bulk of  $\text{Li}_x\text{V}_2\text{O}_5$  were so high that it dominated the  $^7\text{Li}$  NMR signal; therefore, only a slow component was obtained. The transmission electron microscopic images showed that the  $\text{Li}_x\text{V}_2\text{O}_5$  cathode electrode was formed with crystalline particles with size in the range from  $0.5 \mu\text{m}$  to tens  $\mu\text{m}$ . For a particle larger than  $1 \mu\text{m}$ , the ratio of V ions located at the surface and inside the bulk was estimated and was found to be less than 0.3%. For a discharged  $\text{Li}_x\text{V}_2\text{O}_5$  sample ( $1.6 < x < 1.8$ ), the signal from Li ions in the bulk  $\text{Li}_x\text{V}_2\text{O}_5$

sample was higher enough to predominate fast component from Li ions in the electrode surface region. For a charged  $\text{Li}_x\text{V}_2\text{O}_5$  sample ( $0.1 < x < 0.2$ ), the Li ions concentration inside bulk of  $\text{Li}_x\text{V}_2\text{O}_5$  is significantly lower than that at discharged state, the numbers of Li ions in the electrode surface region due to surface reactions such as adsorption became competitive to that inside the bulk, because according to Nernst equation, the concentration of Li ions in the electrode surface region is determined by not only the concentration of V ions at the electrode surface but also the concentration of Li ions in the electrode and the potential of the electrode, which was about 3.4 V vs. Li electrode for charged  $\text{Li}_x\text{V}_2\text{O}_5$  electrode.

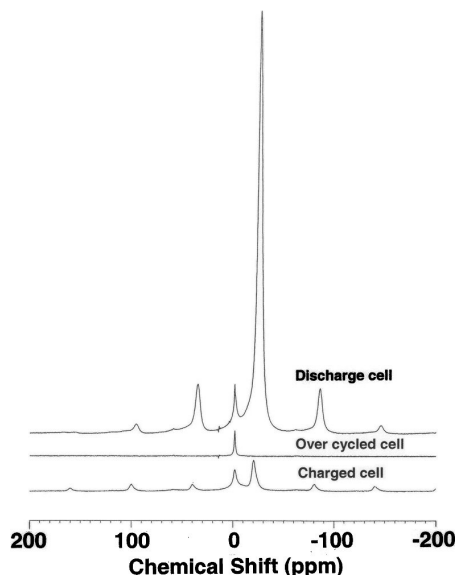


Figure 3:  $^7\text{Li}$  NMR spectra of different  $\text{Li}_x\text{V}_2\text{O}_5$  cathodes at  $25^\circ\text{C}$  and spin rate of 7 kHz.

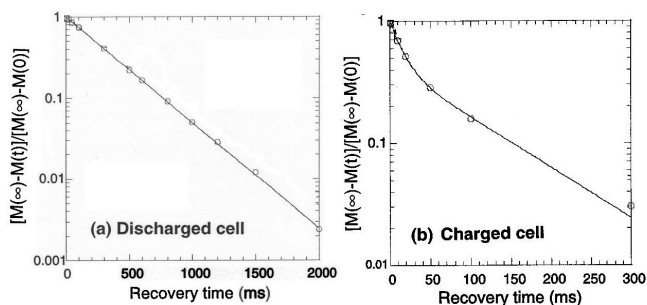


Figure 4: The intensity of  $^7\text{Li}$  NMR signal as a function of time for  $\text{Li}_x\text{V}_2\text{O}_5$  cathodes from (a) a discharged and (b) a charged cells. The lines are theoretical fitting with the exponential decay law.

The  $^{51}\text{V}$  NMR spectral measurements were clearly shown the transition from  $\text{V}^{+5}$  to  $\text{V}^{+4}$  states when Li concentration in-

creased in  $\text{Li}_x\text{V}_2\text{O}_5$  structure. Figure 5 shows that broad signals were obtained from three samples with different charge states using an 833 MHz spectrometer. Asymmetric broadening in  $^{51}\text{V}$  NMR spectra is a combination effects of the dipole interaction which broadens the central transition lines, the quadrupolar interaction which shifted the central lines, and the chemical shielding interaction which changes the position of the lines and makes the asymmetric. Similar signals were obtained from samples from the charged and over-cycled cells. For both samples, the Li concentration in  $\text{Li}_x\text{V}_2\text{O}_5$  was so low that  $\text{V}^{+5}$  species were over dominating. However, for sample from the discharge cell,  $\text{V}^{+4}$  and perhaps even  $\text{V}^{+3}$  species increased with increasing the Li concentration. The paramagnetic  $\text{V}^{+4}$  and  $\text{V}^{+3}$  ions are responsible for the loss of the intensity in  $^{51}\text{V}$  NMR signal [16,17].

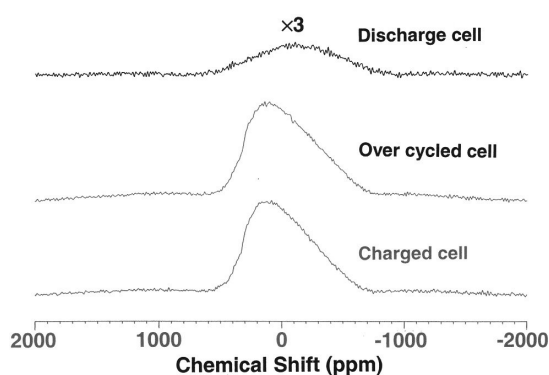


Figure 5: Static  $^{51}\text{V}$  NMR spectra of different  $\text{Li}_x\text{V}_2\text{O}_5$  cathodes at room temperature.

#### 4. CONCLUSION

From  $^7\text{Li}$  NMR spectra and  $T_1$  measurement, three groups of Li ions were observed. They were due to the Li ions from the residual electrolyte and in the electrode surface region as well as inside the bulk of  $\text{Li}_x\text{V}_2\text{O}_5$ . The concentration changes from different groups of Li ions in  $\text{Li}_x\text{V}_2\text{O}_5$  with different charged states were reflected from the magnitude of  $^7\text{Li}$  NMR signals. The width changes from  $^7\text{Li}$  NMR signals were observed as Li intercalation, which produced the conversion of  $\text{V}^{5+}$  to  $\text{V}^{4+}$  (or  $\text{V}^{3+}$ ). From  $^{51}\text{V}$  NMR spectra, it was found that almost identical spectra were obtained from  $\text{Li}_x\text{V}_2\text{O}_5$  at charged and over cycled states, which indicated that the host structure of  $\text{Li}_x\text{V}_2\text{O}_5$  cathode electrode material had no significant change.

We are indebted to Mr. Gov'kov and Dr. Brey of the NMR program at the NHMFL for a support of building the single resonance 4 mm MAS probe. This work was partially support by U.S. Army Communications-Electronics Command and by a Program Enhancement Grant (PEG) (Project # 550240537) from Florida State University.

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