

# 7Li NMR Studies of Electrochemically Lithiated V2O5 Xerogels

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Lithium ions were electrochemically inserted into V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogel and studied with <sup>7</sup>Li magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. Two distinct lithium environments were resolved and assigned to lithium ions occupying either interfacial or intercalated sites in the V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogel matrix. Lithium chemical shifts, relaxation measurements, and variable-temperature (VT) MAS NMR are used to determine the mobility of both interfacial and intercalated lithium ions and the associated coupling to paramagnetic sites on the V<sub>2</sub>O<sub>5</sub> xerogel lattice. From spin-lattice relaxation ( $T_1$ ) data, a minimum is observed, yielding an average polaron correlation time in excellent agreement with a value based independently on conductivity measurements. Thus, revealing that the dominant relaxation mechanism is associated with the nuclear dipole coupling to polaron motion.

## 1. Introduction

Lithium intercalation materials are of technical interest as electrodes for lithium secondary batteries, which require reversible uptake and release of lithium ions. Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>)-based materials are a promising set of positive electrode materials for lithium battery applications.<sup>1,2</sup> Large amounts of lithium ions (Li<sup>+</sup>) can be reversibly inserted between the V<sub>2</sub>O<sub>5</sub> layers. For example, it has been shown that up to 3.3 mol of Li<sup>+</sup> can be incorporated into V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O xerogels.<sup>3,4</sup> This xerogel, which is easily synthesized by sol-gel processes,<sup>5–8</sup> displays efficient electrochemical cycling<sup>9</sup> and has a large specific energy (1137 W h/kg).<sup>3</sup>

V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O xerogels are a semiamorphous material composed of distorted VO<sub>5</sub> polyhedra linked in such a way to form layers separated by water molecules.<sup>10</sup> The degree of hydration ( $n$ ) depends on the drying conditions. A room temperature dried xerogel has a chemical composition of V<sub>2</sub>O<sub>5</sub>·1.6H<sub>2</sub>O while a xerogel dried at 100 °C under vacuum has a composition of V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O. These materials display one-dimensional ordering along the *c*-direction, ⟨00*x2O<sub>5</sub> ribbons<sup>5,11,12</sup> with an average layer spacing of*

11.6 Å for V<sub>2</sub>O<sub>5</sub>·1.6H<sub>2</sub>O and 8.7 Å for V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O. The smaller layer spacing of the V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogel is caused by the removal of water from the interlamellar region.<sup>5</sup>

Lithium ions have been shown to electrochemically intercalate and deintercalate in both crystalline<sup>13</sup> and amorphous<sup>14</sup> V<sub>2</sub>O<sub>5</sub>-based materials. Amorphous forms of V<sub>2</sub>O<sub>5</sub>, such as xerogel and aerogel, have been shown to support intercalation and release rates of Li<sup>+</sup> that are significantly enhanced over comparable crystalline phases.<sup>2</sup> While Li<sup>+</sup> structure and dynamics have been well characterized in chemically lithiated V<sub>2</sub>O<sub>5</sub> bronzes<sup>15–17</sup> and electrochemically lithiated  $\alpha$ - and  $\gamma$ -V<sub>2</sub>O<sub>5</sub>,<sup>18,19</sup> amorphous forms of lithiated V<sub>2</sub>O<sub>5</sub> have gone relatively uncharacterized. In this paper, we present <sup>7</sup>Li solid-state NMR studies that elucidate structural and dynamic features of lithium ions inserted into V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogels. The effect of lithium concentration, temperature, and characterization of various lithium environments is explored. Comparisons are made to crystalline V<sub>2</sub>O<sub>5</sub> hosts to obtain a molecular understanding of differences in lithium ion structure and dynamics.

## 2. Experimental Section

**Synthesis of V<sub>2</sub>O<sub>5</sub> Sol-Gel.** V<sub>2</sub>O<sub>5</sub> sol-gel was prepared as previously reported<sup>5–8</sup> by passing a 0.5 M solution of

- (1) Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651.
- (2) Le, D. B.; Passerini, S.; Guo, J.; Ressler, J.; Owens, B. B.; Smyrl, W. H. *J. Electrochem. Soc.* **1996**, *143*, 2099.
- (3) Park, H. K.; Smyrl, W. H.; Ward, M. D. *J. Electrochem. Soc.* **1995**, *142*, 1068.
- (4) Park, H. K.; Smyrl, W. H. *J. Electrochem. Soc.* **1994**, *141*, L25.
- (5) Livage, J. *Chem. Mater.* **1991**, *3*, 578.
- (6) Nabavi, M.; Sanchez, C.; Livage, J. *Philos. Mag. B* **1991**, *63*, 941.
- (7) Aldebert, P.; Baffier, N.; Legendre, J.; Livage, J. *J. Rev. Chem. Mineral.* **1982**, *19*, 485.
- (8) Livage, J. *Mater. Res. Bull.* **1991**, *26*, 1173.
- (9) West, K.; Zachau-Christiansen, B.; Jacobsen, T.; Skaarup, S. *J. Electrochim. Acta* **1993**, *38*, 1215.
- (10) Stizza, S.; Mancini, G.; Benfatto, M.; Natoli, C. R.; Garcia, J.; Bianconi, A. *Phys. Rev. B* **1989**, *40*, 12229.
- (11) Legendre, J.; Aldebert, P.; Baffier, N.; Livage, J. *J. Colloid Interface Sci.* **1983**, *94*, 84.
- (12) Yao, T.; Oka, Y.; Yamamoto, N. *Mater. Res. Bull.* **1992**, *116*, 279.
- (13) Vivier, V.; Farcy, J.; Pereira-Ramos, J. P. *J. Electrochim. Acta* **1998**, *44*, 831.
- (14) Baddour, R.; Pereira-Ramos, J. P.; Messina, R.; Perichon, J. *J. Electroanal. Chem.* **1990**, *277*, 359.
- (15) Bose, M.; Basu, A. *Solid State Ionics* **1986**, *18/19*, 902.
- (16) Hirschinger, J.; Mongelet, T.; Marichal, C.; Granger, P.; Savariault, J.-M.; Deramond, E.; Galy, J. *J. Phys. Chem.* **1993**, *97*, 10301.
- (17) Rozier, P.; Savariault, J.-M.; Galy, J.; Marichal, C.; Hirschinger, J.; Granger, P. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 1.
- (18) Cocciantelli, J. M.; Suh, K. S.; Sénégas, J.; Doumerc, J. P.; Pouchard, M. *J. Phys. Chem. Solids* **1992**, *53*, 57.
- (19) Cocciantelli, J. M.; Suh, K. S.; Sénégas, J.; Doumerc, J. P.; Soubeiryoux, J. L.; Pouchard, M. *J. Phys. Chem. Solids* **1992**, *53*, 51.

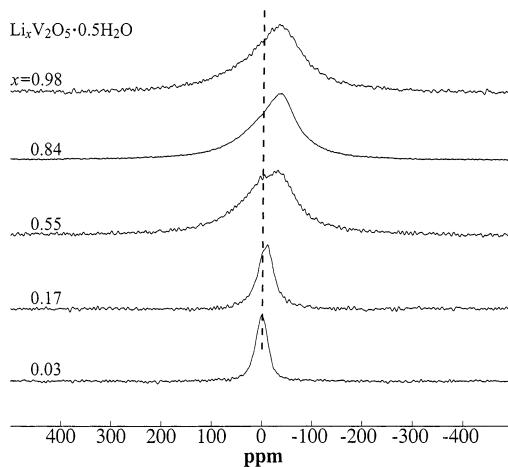
ammonium metavanadate (Aldrich) through an Amberlyst ion-exchange column. Acidification results in a yellow solution, which polymerizes within minutes, resulting in a deep red gel. Excess water was removed with a rotary evaporator by heating at 40 °C. The gels were allowed to age for 2 months at ambient conditions.

**Electrochemistry.** Lithium ion insertion was accomplished by performing potentiostatic step experiments with a Princeton Applied Research (PAR) 273 potentiostat. The working electrode was a stainless steel mesh with a geometrical surface area of 40 cm<sup>2</sup> dip-coated with V<sub>2</sub>O<sub>5</sub> sol–gel. The electrodes were then annealed at 110 °C under vacuum for 15 h to obtain the xerogel form, V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O.<sup>5</sup> The weight of active material following the drying process was typically 50–75 mg. Both the reference and auxiliary electrodes were lithium metal. The electrodes were arranged in a three-chamber cell with each chamber separated from the others by a medium-porosity (25–50 µm) frit. The electrolyte used was 1 M LiClO<sub>4</sub> in propylene carbonate (PC). All the electrochemical experiments were performed in an argon-filled glovebox (Vacuum Atmospheres) to avoid rehydration of the hygroscopic xerogels and moisture contamination of the PC. The open circuit potential was allowed to equilibrate for 20–30 min prior to electrochemical lithium insertion. Lithium ions were inserted by applying potential steps from the initial open circuit potential of 3.8 V to potentials in the range 1.8–3.5 V (vs Li/Li<sup>+</sup>). The lithiated V<sub>2</sub>O<sub>5</sub> xerogel electrodes were rinsed with clean PC to remove supporting electrolyte following the electrochemical process. The electrodes were then placed on a vacuum line at 1 mTorr and 100 °C to remove any remaining PC, as judged by Fourier transform infrared (FT-IR) measurements with a Nicolet Magna-IR 560 spectrometer. The amount of intercalated Li<sup>+</sup> was calculated from the total number of coulombs passed and the original weight of active material by assuming 100% current efficiency. Electrodes were made from crystalline V<sub>2</sub>O<sub>5</sub> by pressing the powder into a piece of stainless steel mesh with a hydraulic press. Electrochemical intercalation conditions were the same as those used for the xerogel samples.

**Solid-State NMR.** NMR measurements were carried out with a Bruker MSL 400 MHz spectrometer employing a 4 mm Bruker VT-MAS probe operating at a <sup>7</sup>Li frequency of 155.5 MHz. The samples were packed in zirconia rotors with O-ring Kel-F caps in an argon-filled glovebox to avoid contamination of the air-sensitive lithiated xerogels. Samples typically weighed 50 mg and required between 100 and 1000 scans depending on the amount of lithium present. A single 90° pulse (3 µs) or a solid echo<sup>20</sup> pulse sequence was applied followed by acquisition of the free induction decay. Spectra were identical for both single pulse and solid echo methods. In the single pulse experiment, a 20 µs acquisition delay was required in order to allow for pulse ring down in the probe. Chemical shifts are reported with respect to an aqueous LiCl reference where the resonant frequency of the aqueous sample was set to 0 ppm. NMR spectra were collected under static and magic angle spinning conditions.<sup>21</sup> The magic angle was set by maximizing the number of <sup>79</sup>Br spinning sidebands in a solid sample of KBr.<sup>22</sup> All MAS experiments were performed at a rotor spinning rate ( $\nu_r$ ) of 10 kHz ± 5 Hz. Spin–lattice (longitudinal) relaxation times ( $T_1$ ) and spin–spin (transverse) relaxation times ( $T_2$ ) were determined from a standard inversion recovery sequence and a Carr–Purcell–Meiboom–Gill sequence, respectively.<sup>23</sup>

### 3. Results and Discussion

<sup>7</sup>Li NMR spectra were collected under both static and MAS conditions to probe the local lithium environment of V<sub>2</sub>O<sub>5</sub> xerogels containing various amounts of electro-



**Figure 1.** Room temperature (300 K) static <sup>7</sup>Li NMR spectra of electrochemically lithiated Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogels. The respective values of  $x$  are indicated in the figure.

chemically intercalated Li<sup>+</sup>. <sup>7</sup>Li static spectra of lithiated V<sub>2</sub>O<sub>5</sub> xerogels are displayed in Figure 1. A single broad asymmetric peak is observed over the entire lithium loading range (Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O, 0.03 ≤  $x$  ≤ 0.98), corresponding primarily to the (1/2 ↔ -1/2) central transition. Distinct satellite transitions (±3/2 ↔ ±1/2) are not apparent in any of the static <sup>7</sup>Li NMR spectra. The peak shifts upfield (to lower frequency) between -3 and -38 ppm and broadens with increasing amounts of inserted Li<sup>+</sup>. The broad line width can be attributed to homonuclear and heteronuclear magnetic dipolar interactions between <sup>7</sup>Li ions and surrounding nuclei as well as hyperfine interactions with unpaired electrons at reduced vanadium metal centers. In addition, second-order quadrupole effects can contribute to broadening of the central transition because of noncubic local symmetry environments.<sup>24</sup> However, the latter will be considered negligible since MAS data presented below show the quadrupole coupling constant to be relatively small. The change in chemical shift with increasing amounts of Li<sup>+</sup> is similar to that in lithiated V<sub>6</sub>O<sub>13</sub><sup>25</sup> and is thought to be caused by a hyperfine interaction between the lithium nuclear moments and the electron moments at the paramagnetic metal centers.<sup>26</sup>

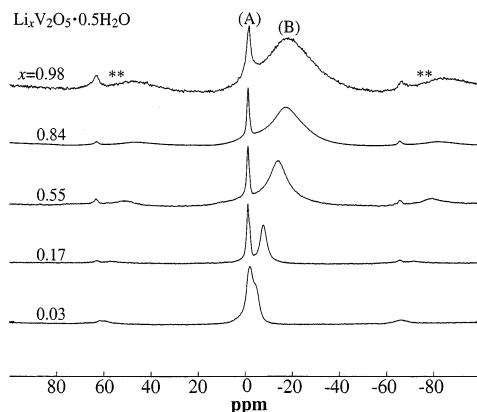
<sup>7</sup>Li MAS NMR spectra of V<sub>2</sub>O<sub>5</sub>·0.5H<sub>2</sub>O xerogel with varying lithium concentration,  $x$ , are shown in Figure 2. Two peaks are resolved: (A) a narrow resonance positioned close to 0 ppm and (B) a broad resonance shifted upfield. Also, weak spinning sidebands (\*\*) corresponding to the satellite transitions are observed at ± $\nu_r$  = 10 kHz. Only two sets of low-intensity spinning sidebands appear in the MAS spectra, allowing estimation of a relatively small quadrupole coupling constant equal to 40 kHz. The upfield peak broadens and shifts further upfield as the amount of inserted lithium is increased while the downfield peak maintains a relatively constant chemical shift and line width across the entire lithiation range. The downfield peak is in the

(20) Powles, J. G.; Mansfield, P. *Phys. Lett.* **1962**, 2, 58.  
 (21) Lowe, I. *Phys. Rev. Lett.* **1959**, 2, 285.  
 (22) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, 48, 125.  
 (23) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR*; Perseus Books: Reading, MA, 1981.

(24) Meadows, M. D.; Smith, K. A.; Kinsey, R. A.; Rothgeb, M. T.; Skarjune, R. P.; Oldfield, E. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, 79, 1351.

(25) Stallworth, P. E.; Kostov, S.; denBoer, M. L.; Greenbaum, S. G.; Lampe-Onnerud, C. *J. Appl. Phys.* **1998**, 83, 1247.

(26) La Mar, G. N.; Horrocks, W. D., Jr.; Holm, R. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.



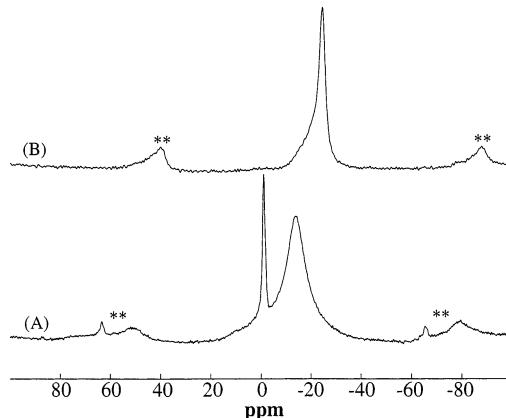
**Figure 2.** Room temperature (300 K)  $^7\text{Li}$  MAS NMR spectra of lithiated  $V_2\text{O}_5\cdot 0.5\text{H}_2\text{O}$  xerogels. A spinning speed,  $\nu_r$ , of 10 kHz was used for all samples. Two resonances are resolved and assigned to (A) surface-bound ion-exchangeable and (B) intercalated  $\text{Li}^+$  sites. Satellite transitions are resolved as spinning sidebands and marked with a double asterisk (\*\*).

typical chemical shift range for ionic lithium, and the line width indicates that its coupling to the lattice is averaged by MAS and that these ions are in a homogeneous environment. The upfield peak shifts out of the typical range for ionic lithium indicating a stronger coupling to paramagnetic electrons at  $\text{V}^{4+}$  sites on the lattice.

The two resolved lithium peaks shown in Figure 2 are attributed to (A) lithium ions at interfaces within the  $V_2\text{O}_5$  xerogel material and (B) lithium ions intercalated between the  $V_2\text{O}_5$  layers. Upon initial lithiation ( $x = 0.03$ ), the MAS NMR spectrum reveal only one asymmetric peak at  $\sim 0$  ppm. Thus, the majority of lithium ions at this low lithium loading are at the interface with a small amount just beginning to enter the interlayer region. When  $x$  is increased to 0.17, the lithium ions occupy both the interfacial and interlayer regime to the same degree ( $\sim 50:50$  peak areas). As  $x \geq 0.55$  is approached, it appears that the interfacial sites are saturated, and only the interlayer region continues to fill with lithium ions. The assignment of the two lithium ion sites in the MAS NMR spectra to intercalated and interfacial lithium is further supported by variable temperature (VT) NMR analysis, comparison to lithiated crystalline  $V_2\text{O}_5$  NMR spectra, and  $T_1$  relaxation measurements.

The upfield chemical shift observed in the static and MAS NMR of lithiated  $V_2\text{O}_5\cdot 0.5\text{H}_2\text{O}$  xerogel is ascribed to the hyperfine interaction between the lithium nuclei and paramagnetic  $\text{V}^{4+}$  sites on the lattice. Diamagnetic lithium containing compounds have a small shift range between  $-9$  and  $3$  ppm.<sup>27</sup> The relatively larger shifts observed in our samples as well as lithiated  $V_2\text{O}_5$  crystalline phases are attributed to an increasing population of paramagnetic  $\text{V}^{4+}$  species with increasing lithium concentration. The lithium nuclei couple with the unpaired electrons, causing what we interpret to be a paramagnetic shift.

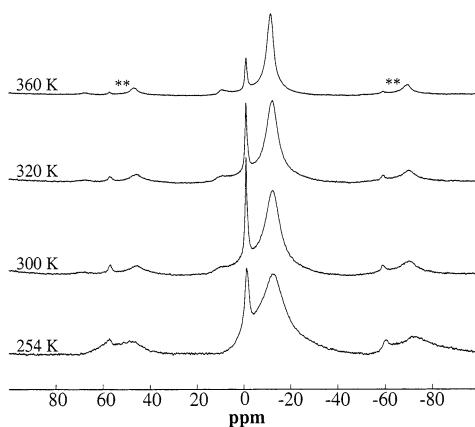
There are three mechanisms that can result in a paramagnetic shift: (1) the Fermi-contact interaction, (2) the dipolar pseudocontact interaction, and (3) an interaction with conduction electrons (Knight shift).<sup>26</sup>



**Figure 3.**  $^7\text{Li}$  MAS NMR spectra of room temperature (300 K) (A)  $\text{Li}_{0.55}\text{V}_2\text{O}_5\cdot 0.5\text{H}_2\text{O}$  xerogel and (B) crystalline  $\text{Li}_{0.55}\text{V}_2\text{O}_5$ . The spinning speed was 10 kHz, and spinning sidebands are indicated by asterisks.

The Knight shift is typically reserved to describe the large chemical shifts in metals due to conduction electrons that have a high probability of being at the nucleus.<sup>28</sup> The  $^7\text{Li}$  shifts observed in this study are not considered to be Knight shifted since the paramagnetic electrons are primarily localized on the  $\text{V}_2\text{O}_5$  lattice and do not have a high probability of being at the lithium nucleus. The  $\text{V}_2\text{O}_5$  xerogel is a mixed valence semiconductor where electron transport occurs by a polaron hopping process.<sup>29</sup> The direct band gap<sup>30</sup> of  $\text{V}_2\text{O}_5$  is 2.3 eV, indicating essentially no population of the conduction band in the temperature range studied here. Furthermore, a Knight shift is typically to higher frequency,<sup>31</sup> while the shift observed here is to lower frequency. The Fermi-contact shift results from a through-bond interaction that transfers electron density from the paramagnetic site to the observed nuclei. This type of shift has been observed in lithium manganate positive electrode materials<sup>32–35</sup> and can be quite large (100's to 1000's of ppm). The Fermi-contact shift also typically follows a Curie law. The pseudocontact shift results from a through-space dipolar interaction, and the observed shifts are typically smaller than shifts resulting from a Fermi-contact interaction. The pseudocontact shift does not necessarily follow a  $1/T$ , Curie law dependence.<sup>36</sup> Considering the shift observed in these  $\text{Li}_x\text{V}_2\text{O}_5\cdot 0.5\text{H}_2\text{O}$  xerogels do not follow a Curie law (see Figure 4), we conclude that the observed lithium chemical shift is dominated by a pseudocontact interaction. Further justification for interpreting the observed lithium NMR shifts as arising from a pseudocontact mechanism comes from a study by Galy et al.<sup>16</sup> on high-temperature phases of  $\text{V}_2\text{O}_5$  bronzes. In this study, chemical shifts

(28) Townes, C. H.; Herring, C.; Knight, W. D. *Phys. Rev.* **1950**, 77, 852.  
 (29) Triberis, G. P. *J. Non-Cryst. Solids* **1988**, 104, 135.  
 (30) Chakrabarti, A.; Hermann, K.; Druzinic, M.; Witko, M.; Wagner, F.; Petersen, M. *Phys. Rev. B* **1999**, 59, 10583.  
 (31) Slichter, C. P. *Principles of Magnetic Resonance*; Springer-Verlag: Berlin, 1990.  
 (32) Lee, Y. J.; Wang, F.; Grey, C. P. *J. Am. Chem. Soc.* **1998**, 120, 12601.  
 (33) Lee, Y. J.; Wang, F.; Mukerjee, S.; McBreen, J.; Grey, C. P. *J. Electrochem. Soc.* **2000**, 147, 803.  
 (34) Tucker, M. C.; Reimer, J. A.; Cairns, E. J. *Electrochem. Solid-State Lett.* **2000**, 3, 463.  
 (35) Tucker, M. C.; Reimer, J. A.; Cairns, E. J. *J. Electrochem. Soc.* **2001**, 148, A951.  
 (36) Bleaney, B. *J. Magn. Reson.* **1972**, 8, 91.



**Figure 4.** Variable temperature  $^7\text{Li}$  MAS NMR spectra of  $\text{Li}_{0.55}\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  xerogel. The spinning rate was 10 kHz for all spectra.

for  $\beta$ ,  $\beta'$ , and  $\gamma$  phases of  $\text{LiV}_2\text{O}_5$  were determined to be dominated by a dipolar, pseudocontact shift mechanism.

The line width of both static and MAS  $^7\text{Li}$  NMR peaks significantly broadens with increased amounts of electrochemically inserted lithium. This is most evident in the MAS NMR peak associated with intercalated lithium and is likely the result of (i) an increase in dipolar coupling (not averaged by MAS) or (ii) an increased distribution of lithium environments in the semiamorphous xerogel. While lithiation of  $\text{V}_2\text{O}_5$  xerogel is known to lower the degree of structural order,<sup>37</sup> the latter of the two possibilities is less likely since  $T_2$  relaxation measurements indicate the line width to be homogeneously broadened. The  $T_2$  measured for the broad component under MAS yields a value which relates to the observed line width. For example, the xerogel sample with  $x = 0.55$  had a  $T_2$  of 180  $\mu\text{s}$ , which compares well with the 1.5 kHz line width of the broad component. The Li–Li and Li–V dipolar couplings were estimated from crystalline  $\text{Li}_x\text{V}_2\text{O}_5$  distances to be 5 and 3.3–5.2 kHz, respectively.<sup>38</sup> Both of these interactions should be averaged by MAS. This leaves the Li–H and Li–e<sup>-</sup> dipolar couplings to consider. The Li–H interaction is difficult to determine since little is known about the position of water in this semiamorphous system. However, because the  $^7\text{Li}$  MAS NMR spectra of a perdeuterated sample and the proton-containing sample are identical, it was concluded that the Li–H heteronuclear dipole coupling is completely averaged by MAS. The number of paramagnetic  $\text{V}^{4+}$  sites increases as the amount of lithium is increased. Therefore, the observed increase in line width is consistent with an increased dipolar coupling between the lithium nuclei and the unpaired electrons (Li–e<sup>-</sup>) on the  $\text{V}_2\text{O}_5$  xerogel lattice. Besides broadening, the peak also continues to shift upfield with increasing lithium concentration. This too is consistent with an increasing amount of paramagnetic species being formed at higher lithium loading.

The changes in  $^7\text{Li}$  chemical shift and line width at high lithium concentrations have primarily been ascribed to a hyperfine coupling between lithium ions and paramagnetic electrons on the  $\text{V}_2\text{O}_5$  lattice. Lithium ion dynamics could also account for some of the observed

variations. The self-diffusion coefficient of lithium ions in  $\text{V}_2\text{O}_5$  xerogel has been shown to decrease up to 2 orders of magnitude in the concentration range studied here ( $x \leq 1$ ), as the lithium population is increased.<sup>39,40</sup> The mobility of the observed nuclei ( $^7\text{Li}$ ) is known to have a large effect on  $T_2$  and therefore the line width.<sup>41</sup> As the amount of inserted lithium increases, the lithium mobility is hindered due to crowding in the interlamellar region and a decrease in site availability. This results in the  $^7\text{Li}$  nuclei experiencing stronger dipolar, quadrupolar, and hyperfine interactions. Therefore, we attribute the observed broadening in both the static and MAS spectra to the increasing population of paramagnetic sites coupled with a decrease in lithium mobility.

Spectra of lithiated  $\text{V}_2\text{O}_5$  (A) xerogel and (B) crystalline material both containing 0.55 mol of lithium are displayed in Figure 3. The difference in magnitude of the observed paramagnetic shift between the xerogel and crystalline samples can be explained by considering variations in the lithium environment resulting from the lithium intercalation process. The  $^7\text{Li}$  chemical shift in crystalline  $\text{Li}_x\text{V}_2\text{O}_5$  materials is dependent on structural phase changes which occur during ion insertion.<sup>18,19</sup> Intercalation of lithium ions causes the crystalline material to undergo structural distortions that result in a decrease in the  $a$  lattice parameter and an increase in the  $c$  lattice parameter as  $x$  approaches unity.<sup>42</sup> This has been described by Galy et al.<sup>38</sup> as a “puckering” in the layers that results in lithium ions being in a more tetrahedral-like environment as the  $\delta$  phase is formed at  $x = 1$ . The crystalline form  $\text{Li}_{0.55}\text{V}_2\text{O}_5$ , presented in Figure 3, is a mix of two phases the  $\epsilon 1$  phase at -25 ppm and the  $\epsilon 2$  phase at -22 ppm.<sup>17</sup> The  $\text{V}_2\text{O}_5$  lattice remains essentially unchanged in the  $\epsilon$  phases with lithium coordinated to a trigonal prism of oxygens.<sup>38</sup> Since the local structure of  $\text{V}_2\text{O}_5$  xerogel is thought to be close to the crystalline form,<sup>8</sup> some comparisons can be made between the  $^7\text{Li}$  NMR chemical shift of the xerogel and those previously observed in the crystal. In the crystalline forms, a sample with  $x = 0.9$  displays a  $^7\text{Li}$  resonance shift downfield to -12 ppm representing the  $\delta$  phase with a small signal at 5 ppm corresponding to the  $\gamma$  phase.<sup>18</sup> The puckering in the layers that occurs in the  $\delta$  phase results in  $\text{Li}^+$  in a tetrahedral environment, while in the  $\gamma$  phase  $\text{Li}^+$  occupies a distorted octahedral environment where the  $\text{VO}_5$  pyramids have a different alternating arrangement.<sup>43</sup> If either of these phase changes occurred in the xerogel material, a downfield shift would be expected. The broad resonance (B) in the xerogel MAS spectra (see Figure 2) shifts upfield continuously across the entire lithium loading range with no evidence of a shift back downfield. This indicates that neither of these phase changes occurs in the xerogel material in the lithium composition range studied.

(39) Holland, G. P.; Huguenin, F.; Torresi, R. M.; Buttry, D. A. *J. Electrochem. Soc.*, submitted for publication.

(40) Baddour, R.; Pereira-Ramos, J. P.; Messina, R.; Perichon, J. *J. Electroanal. Chem.* **1991**, *81*, 314.

(41) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.

(42) Cocciantelli, J. M.; Doumerc, J. P.; Pouchard, M.; Broussely, M.; Labat, J. *J. Power Sources* **1991**, *34*, 103.

(43) Stallworth, P. E.; Johnson, F. S.; Greenbaum, S. G.; Passerini, S.; Flowers, J.; Smyrl, W.; Fontanella, J. *J. Solid State Ionics* **2002**, *146*, 43.

(37) Cazzanelli, E.; Mariotto, G.; Passerini, S.; Smyrl, W. H. *J. Non-Cryst. Solids* **1996**, *208*, 89.

(38) Galy, J. *J. Solid State Chem.* **1992**, *100*, 229.

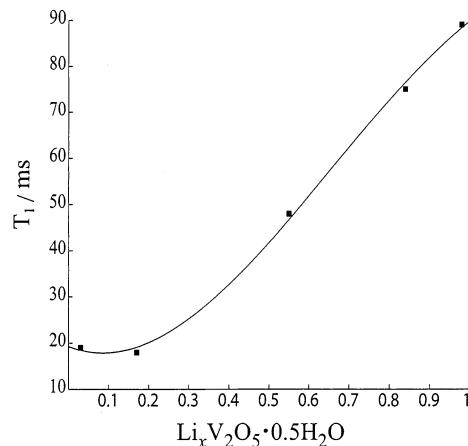
The most notable difference between the crystalline and xerogel lithiated  $V_2O_5$  NMR spectra, shown in Figure 3, is the absence of a downfield narrow peak in the crystalline spectrum. This narrow resonance centered near 0 ppm, which we assign to interfacial lithium ions, does not appear in any of the known crystalline  $Li_xV_2O_5$  samples.<sup>18,19</sup>  $^7Li$  MAS  $T_1$  measurements of  $Li_{0.55}V_2O_5 \cdot 0.5H_2O$  xerogel result in a  $T_1$  of  $20 \pm 2$  and  $115 \pm 10$  ms for the intercalated and interfacial lithium components, respectively. Compared to the  $T_1$  of common lithium salts and lithium in SEI films which are typically  $\geq 1$  s,<sup>44</sup> the relatively shorter  $T_1$  relaxation time of both resonances indicates that neither peak results from an impurity phase (i.e., SEI,  $LiClO_4$ , or  $Li_2O$ ). This is further verified by solvent rinsing experiments where an electrode soaked in clean PC for 2 days shows no variation in the intensity of either resonance. NMR peaks resulting from SEI films have been shown to decrease in intensity and disappear when washed with clean solvent.<sup>44</sup> Thus, the interfacial lithium NMR peak seem to be due to features that are unique to the xerogel material. The synthesis of  $V_2O_5$  sol–gel via acidification of vanadate salts results in 1%  $V^{4+}$  sites.<sup>5</sup> These reduced metal centers are charge compensated by acidic protons at the oxide–water interface.<sup>8</sup> When the sol–gel is dried to its xerogel form, hydronium ions can be exchanged for alkali metal cations by dipping the film in a PC solution containing the desired salt.<sup>40,45</sup> The narrow resonance observed in the  $^7Li$  MAS NMR spectra can be attributed to  $Li$  ions that exchange with hydromium ions prior to electrochemical intercalation. The narrow resonance is the only resonance that appears in the  $^7Li$  MAS NMR spectra when an electrode is dipped in the  $LiClO_4$  containing electrolyte without performing electrochemical reduction.

Ion-exchange experiments were performed to help verify that the narrow resonance located at 0 ppm represents charge compensated sites located at interfaces of the xerogel material opposed to in the interlayer region. Reduced samples were dipped in  $NaClO_4$  containing electrolyte to follow the exchange process. The narrow peak disappears very rapidly with little change to the broad resonance. This is consistent with ESR data which implies that these charge-compensated  $V^{4+}$  sites are located at the surface of the xerogel particles and are therefore more available for exchange than intercalated  $Li^+$ .<sup>46</sup> The characteristics of the narrow resonance are representative of this surface environment. The short  $T_1$  observed is an indication of its location near  $V^{4+}$  sites while its narrow line width compared to the broad resonance could result from more rapid motion at the surface. In addition, the narrow resonance does not decrease in intensity upon deintercalation while the broad resonance completely disappears. Therefore, the broad and narrow resonance are assigned to electrochemically active intercalated  $Li^+$  and electrochemically inactive charge compensated  $Li^+$  at the xerogel interface, respectively.

(44) Wang, Y.; Guo, X.; Greenbaum, S.; Lui, J. *Electrochim. Solid-State Lett.* **2001**, *4*, A68.

(45) Znaidi, L.; Baffier, N.; Lemordant, D. *Solid State Ionics* **1988**, *28–30*, 1750.

(46) Barbonneau, F.; Barboux, P.; Josien, F. A.; Livage, J. *J. Chim. Phys.* **1985**, *82*, 761.

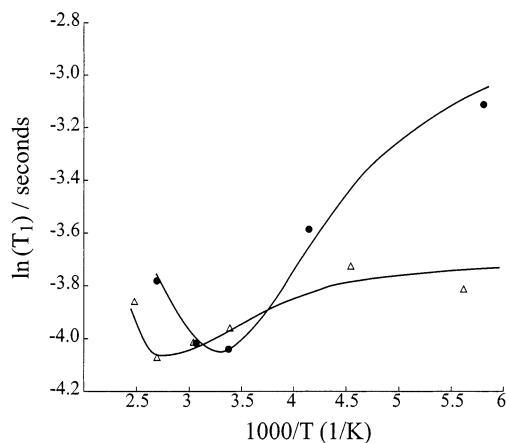


**Figure 5.**  $T_1$  relaxation times measured at (300 K) (■) as a function of  $x$  for  $Li_xV_2O_5 \cdot 0.5H_2O$  xerogel. The line represents a second-order polynomial fit of the data.

Variable temperature (VT)  $^7Li$  MAS NMR experiments were performed to probe the variation in lithium dynamics. It is assumed that the couplings contributing to the observed line widths do not change with temperature; therefore, variations in the line width can be attributed to motional averaging. A stack plot of the MAS spectra at different temperatures is shown in Figure 4 for a sample containing 0.55 mol of  $Li^+$  per mol of  $V_2O_5$  xerogel. A strong sharpening is observed for the intercalated lithium resonance as temperature is increased, characteristic of motional narrowing.<sup>41</sup> Conversely, the interfacial lithium resonance at  $\sim 0$  ppm is narrow above room temperature and only broadens at low temperature. We interpret this to indicate that the intercalated lithium has significantly slower dynamics compared to the interfacial lithium ions. With much slower dynamics, the intercalated lithium becomes susceptible to dipolar broadening, specifically from paramagnetic electrons at reduced metal centers. This interpretation is supported by longer measured  $T_2$  relaxation times for the interfacial lithium peak, indicating more rapid dynamics, a smaller paramagnetic coupling, and hence less broadening as compared to that of interlayer lithium ions.

The VT  $^7Li$  MAS NMR spectra display a variation in the intensity of the narrow resonance as the temperature is increased. Specifically, the narrow resonance decreases with increasing temperature while a small peak grows in at about 10 ppm. This is evidence of a third site in the xerogel matrix that is only resolved at higher temperatures. The loss in intensity of the narrow peak could result from exchange to this new site at 10 ppm or to the interlayer site (broad resonance). The reversibility in the various peak intensities with temperature indicates an exchange process and not a permanent structural modification. Two-dimensional exchange spectroscopy is currently being pursued in our laboratory to better understand this process.

A plot of  $T_1$  relaxation times as a function of  $x$  ( $Li_xV_2O_5 \cdot 0.5H_2O$ ) is shown in Figure 5. Measurements were made under static conditions at 300 K, and the resulting recovery profiles fit a single-exponential function. It should be noted that these  $T_1$  values reflect an average of the two  $T_1$ 's calculated from MAS data for the two distinct sites. Two components were not resolved



**Figure 6.** Natural logarithm of  $T_1$  vs inverse temperature for  $x = 0.03$  ( $\Delta$ ) and  $x = 0.17$  ( $\bullet$ )  $\text{Li}_x\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  xerogels. The solid lines represent the best spline fits to the experimental data and are included as a guide to the eye.

when the inversion recovery data were collected, indicating that the two peaks are significantly convoluted under static conditions.  $T_1$  is observed to increase with increasing lithium concentration. This is surprising considering the electrochemical lithium insertion process occurs via reduction of diamagnetic  $\text{V}^{5+}$  ( $3\text{d}^0$ ) to paramagnetic  $\text{V}^{4+}$  ( $3\text{d}^1$ ). The presence of paramagnetic spins typically results in spin-lattice quenching, and  $T_1$  decreases as the paramagnetic spin concentration increases.<sup>26</sup> This is not always the case, however. A trend displaying an increase in  $T_1$  with increasing lithium concentration, and therefore  $\text{V}^{4+}$  presence, was also observed in chemically lithiated  $\text{V}_6\text{O}_{13}$  in a similar lithium concentration range.<sup>25</sup>

$T_1$  was measured at various temperatures to elucidate the dominant relaxation mechanism and explain why  $T_1$  increases with lithiation ( $x$ ). When  $\ln(T_1)$  is plotted as a function of inverse temperature, as shown in Figure 6, a minimum will occur where the dominant relaxation mechanism is fluctuating at the same frequency as the Larmor precession.<sup>47</sup> The time associated with the specific fluctuation is called the correlation time ( $\tau_c$ ), and a  $T_1$  minimum occurs when  $\omega\tau_c \approx 1$ , where  $\omega = 2\pi\nu_L$  and  $\nu_L$  is the Larmor frequency. A  $T_1$  minimum was observed for two lithiated  $\text{V}_2\text{O}_5$  xerogels containing  $x = 0.03$  and  $0.17$  mol of lithium. The minimum occurs about room temperature ( $\sim 300$  K) for the sample containing  $0.17$  mol of lithium while the sample with  $x = 0.03$  has a minimum shifted to higher temperature ( $\sim 350$  K). The two possible motions that could govern the relaxation process are associated with (i) lithium translational motion ( $\tau_c^{\text{Li}}$ ) or (ii) the electron hopping between the mixed valence states ( $\tau_c^{\sigma}$ ). The correlation time resulting from lithium self-diffusion can be approximated from the following equation:<sup>41</sup>

$$\tau_c^{\text{Li}} = \frac{d^2}{2D} \quad (1)$$

where  $d$  is the mean lithium hopping distance and  $D$  is the self-diffusion coefficient. The  $d$  employed here will be the  $b$ -lattice parameter (3.6 Å) from XRD measure-

**Table 1.** Room Temperature (300 K) Lithium Ion ( $\tau_c^{\text{Li}}$ ) and Electron Hopping ( $\tau_c^{\sigma}$ ) Correlation Times in  $\text{Li}_x\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  Xerogel Calculated from Diffusivity ( $D$ ) and Conductivity ( $\sigma_{\text{dc}}$ ) Data

$x$	$D$ ( $\text{cm}^2 \text{s}^{-1}$ )	$\sigma_{\text{dc}}$ ( $\Omega^{-1} \text{cm}^{-1}$ )	$\tau_c^{\text{Li}}$ (s)	$\tau_c^{\sigma}$ (s)
0.03	$1.23 \times 10^{-9}$	$4 \times 10^{-5}$	$5.27 \times 10^{-7}$	$4.43 \times 10^{-8}$
0.17	$2.11 \times 10^{-10}$	$2 \times 10^{-3}$	$3.07 \times 10^{-6}$	$8.85 \times 10^{-10}$

ments on crystalline  $\text{V}_2\text{O}_5$ .<sup>38</sup> Lithium diffusion coefficients in  $\text{V}_2\text{O}_5$  xerogel have been obtained by applying the galvanostatic intermittent titration technique (GITT).<sup>39,48</sup> There is a concern regarding diffusion coefficients obtained by the GITT method regarding proper estimation of the surface area at the electrolyte/electrode interface.<sup>49</sup> In the previous study,<sup>39</sup> BET (Beunauer, Emmett, and Teller) was used to obtain the xerogel surface area; therefore, the diffusion coefficients are believed to be relatively accurate. The calculated diffusion coefficients resulted in a large correlation time,  $\omega\tau_c^{\text{Li}} \gg 1$ , indicating that lithium translational motion is not the cause of the observed  $T_1$  minimum.

The other possible fluctuation that could be responsible for the observed  $T_1$  minima is the electron hopping between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  sites. It has previously been shown that the electronic conduction in  $\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  xerogel is dominated by polaron hopping.<sup>50</sup> The electron transfer between mixed valence states has been described as a small polaron hopping process where the conductivity follows an Arrhenius law at temperatures above 220 K.<sup>51</sup> The polaron hopping between the different valence states becomes more rapid when the  $\text{V}^{4+}/\text{V}^{5+}$  ratio approaches one, thereby increasing the observed conductivity.<sup>29</sup> The correlation time associated with this polaron mobility ( $\tau_c^{\sigma}$ ) can be calculated from dc conductivity ( $\sigma_{\text{dc}}$ ) measurements<sup>51</sup> by employing the following equation:<sup>52</sup>

$$\tau_c^{\sigma} = \frac{\epsilon_0}{M_{\infty}\sigma_{\text{dc}}} \quad (2)$$

where  $\epsilon_0$  is the permittivity of free space and the electric modulus,  $M_{\infty}$ , is the inverse dielectric constant measured at frequencies much higher than  $(2\pi\tau_c^{\sigma})^{-1}$ . Using the known dielectric properties of  $\text{V}_2\text{O}_5$  xerogels,<sup>53</sup> the electronic correlation time was estimated.

Table 1 summarizes the parameters used to calculate the correlation times associated with lithium and polaron hopping at  $x = 0.03$  and  $x = 0.17$  in  $\text{Li}_x\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  xerogels. The  $T_1$  minimum, where  $\omega\tau_c \approx 1$ , was found to correspond to the polaron hopping between mixed valence sites. As expected, the  $T_1$  minimum shifts to higher temperature for a sample containing less lithium ( $x = 0.03$ ). When the temperature-dependent conductivity<sup>51</sup> is taken into account, the correlation time calculated for the xerogel with  $x = 0.03$  at 350 K is

(48) Weppner, W.; Huggins, R. A. *J. Electrochem. Soc.* **1977**, *124*, 1569.

(49) Leroux, F.; Goward, G.; Power, W. P.; Nazar, L. F. *J. Electrochem. Soc.* **1997**, *144*, 3886.

(50) Murawski, M.; Sanchez, C.; Livage, J.; Audiere, J. P. *J. Non-Cryst. Solids* **1990**, *124*, 71.

(51) Barboux, P.; Baffier, N.; Morineau, R.; Livage, J. *Solid State Protonic Conductors III*; Odense University Press: 1985.

(52) Angell, C. A. *Chem. Rev.* **1990**, *90*, 523.

(53) Badot, J. C.; Fourrier-Lamer, A.; Baffier, N. *J. Phys. (Paris)* **1985**, *46*, 2107.

comparable to the value obtained for the xerogel with  $x = 0.17$  at 300 K. This shows that the observed  $T_1$  minimum is due to coupling between the Li nuclei and polaron motion in the  $V_2O_5$  lattice. Furthermore, samples containing larger amounts of lithium appeared to be dispersionless, and no minimum was observed in the temperature range shown in Figure 6. We believe this is due to the additional complication of other relaxation processes. A clear  $T_1$  minimum is only observed when there is one dominant relaxation process.<sup>47</sup>

Returning to Figure 5, we can now explain the observed increase in  $T_1$  as a function of  $x$  by considering the polaron mobility. As previously shown, the dominant relaxation mechanism is associated with polaron motion. As the lithium concentration increases, so does the  $V^{4+}/V^{5+}$  ratio. This causes an increase in conductivity (while  $x \leq 1$ ) and therefore an increase in  $\tau_c^o$ .<sup>5,29,51</sup> The result is a less efficient coupling of the lithium spin to the  $V_2O_5$  paramagnetic lattice, presumably due to more delocalization of the electrons.

#### 4. Conclusion

This study has yielded significant information regarding the local lithium environment in  $V_2O_5$  xerogel hosts.

$^7\text{Li}$  MAS NMR has been used to resolve two distinct lithium environments which have different dynamic properties as revealed by VT NMR experiments. The two resonances have been assigned to lithium ions that reside at the interface and those that are intercalated in the interlayer region.  $T_1$  relaxation measurements revealed an unusual trend in which the relaxation time lengthens with increasing numbers of paramagnetic  $V^{4+}$  metal centers. This has been explained as an increase in the delocalization of polarons across the  $V_2O_5$  sheets with increasing amounts of lithium.

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