COMPUTATIONAL, ELECTROCHEMICAL AND $^7$Li NMR STUDIES OF LITHIATED DISORDERED CARBON ELECTRODES IN LITHIUM ION CELLS

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COMPUTATIONAL, ELECTROCHEMICAL AND $^7$Li NMR STUDIES OF LITHIATED DISORDERED CARBONS ELECTRODES IN LITHIUM ION CELLS

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ABSTRACT

Disordered carbons that deliver high reversible capacity in electrochemical cells have been synthesized by using inorganic clays as templates to control the pore size and the surface area. The capacities obtained were much higher than those calculated if the resultant carbon had a graphitic-like structure. Computational chemistry was used to investigate the nature of lithium bonding in a carbon lattice unlike graphite. The lithium intercalated fullenerene Li$_n$C$_{60}$ was used as a model for our (non-graphitic) disordered carbon lattice. A dilithium-C$_{60}$ system with a charge and multiplicity of (0,1) and a trilithium-C$_{60}$ system with a charge and multiplicity of (0,4) were investigated. The spatial distribution of lithium ions in an electrochemical cell containing this novel disordered carbon material was investigated *in situ* by Li-7 NMR using an electrochemical cell that was incorporated into a toroid cavity nuclear magnetic resonance (NMR) imager. The concentration of solvated Li$^+$ ions in the carbon anode appears to be larger than in the bulk electrolyte, is substantially lower near the copper/carbon interface, and does not change with cell charging.

INTRODUCTION

High capacity (855 mAh/g), reversible, lithium intercalated carbon anodes were prepared using pillared clays as templates and pyrene, styrene, trioxane/propylene, propylene and ethylene [1,2], that exceed the capacity for stage 1 lithium intercalated carbon anodes (372 mAh/g). Dresselhaus refers to stage 1 Li intercalated graphite compounds as a $\sqrt{3} \times \sqrt{3}$ structure of Li ions on a honeycomb lattice [3]. The spacing between the lithium ions in such a lattice is 4.2 Å. In order to account for or rationalize the high capacity lithium carbon anode materials synthesized in our laboratory, we chose to investigate lithium bonding and spacing in endrohedral lithium complexes of C$_{60}$. Optimized geometries for these systems suggest two types of lithium atoms within the C$_{60}$ lattice. Ionic lithium is obtained for dilithium-C$_{60}$ and covalent lithium for trilithium-C$_{60}$. In both cases, the calculated lithium-lithium separation of 2.96 Å or less is consistent with that required to achieve a specific capacity greater than that obtained in a stage 1 lithium intercalated graphite.

To study the spatial distribution of lithium ions in an electrochemical cell containing this novel carbon material, *in situ* Li-7 nuclear magnetic resonance (NMR) was used. *In situ* NMR methods have been developed to study mobilities, distributions, redox reactions, physicochemical environments, and other properties of the charge carriers and support materials in functioning electrochemical cells [4]. The toroid cavity/electrochemical cell NMR probe used in the present study is capable of recording high resolution spectra for fluid samples and wide line spectra for solid materials, at any position from the central conductor of the toroid cavity (the working electrode of the electrochemical cell). The radiofrequency (rf) magnetic field, $B_1$, generated by the toroid cavity in the sample volume is inhomogeneous, but precisely defined as $B_1 = A/r$, where A is a constant and r is the radial position from the central conductor [5]. Therefore, a single rf pulse of fixed duration results in a 90° rotation of the nuclear magnetization located only at one radial position. We take advantage of the well-defined $B_1$ inhomogeneity to form one-dimensional images. These images
represent radial concentration profiles of the chemical species in the electrochemical cell that are associated with the NMR resonances in a conventional NMR spectrum. For example, the 5% dispersion in Li-7 nutation frequencies across a 100 μm layer at the surface of the carbon coated working electrode reported here is used to record 7Li NMR spectra at three different radial positions within the 100 μm layer. Since the gradient of the B₁ field (VB₁ = -A/r²) is not constant, the radial spacing between NMR spectra is also not constant. A one-dimensional radial concentration image or profile for any chemical species observed in the NMR spectrum is obtained by plotting the intensity or integral of the resonance versus the radial position at which the spectrum was recorded.

The capacity and power output of an electrochemical cell relies, in part, on the presence of electrolyte at all of the accessible surface area of the carbon particles. In this work, we report the in situ 7Li NMR image of solvated lithium ions in an electrolyte wetting a carbon electrode that was derived from pillared clays as templates and pyrene, styrene, trioxane, propylene and ethylene as the organic precursor [1,2]. The carbon was coated onto the central conductor of a toroid cavity detector and served as the cathode electrode in the electrochemical cell.

EXPERIMENTAL

The synthesis of the calcined pillared clays (PILCs) as well as the loading with pyrene, styrene, trioxane/pyrene, ethylene and propylene carbon precursors, has been described in detail elsewhere [1,2]. Electrochemical characterization of the carbon anodes was performed using an Arbin 2400 station cell cycler. Details regarding the preparation of the electrode were described by Sandi et al. [6].

Gaussian 94 was used for all ab initio calculations [7]. Geometry optimizations were performed using the Hartree-Fock method with a 3-21G basis set. However, for the Li₃-C₆₀ complex, the restricted open-shell-Hartree-Fock (ROHF) method was used in order to avoid spin contamination.

For the NMR experiments, approximately 1.0 g of electrolyte (1M LiPF₆ in ethylene carbonate:diethyl carbonate) was placed in a cylindrical electrochemical cell that formed part of the toroid cavity NMR detector. The cell was assembled from a glass tube with an inside diameter of 10.4 mm and length 22.0 mm. Circular rubber septa were used to seal the tube at both ends. A gold wire counter electrode 1.0 mm in diameter was formed into a 7-turn helix and placed against the inner wall of the glass tube. A 0.62 mm diameter copper wire served as a working electrode and passed through the center axis of the cell, piercing both septa. Each end of the working electrode was soldered to a copper rod for mounting the cell in the NMR detector. The working electrode also functioned as the central conductor of the NMR detector. The carbon-based material was made into a slurry as described previously [1,2,6]. The sealed end of a capillary tube was used to coat the working electrode, as it was rapidly rotated in a horizontal orientation, with a thin layer of the cathode material. Between thin-layer coatings the electrode was heated for 20 minutes in air at 170°C. The final diameter and length of the carbon electrode was 2.0 mm and 10.8 mm, respectively. The total mass and area of the active material was 10 mg and 0.7 cm², respectively. The carbon electrode was heated at 80°C under vacuum prior to incorporation into the electrochemical cell. The cell was charged under potentiostatic control from 0.5 to 4.0 V vs. a gold electrode using an EG&G 273A potentiostat. High-resolution 7Li NMR spectra and images were recorded with a home-built toroid cavity probe using a Varian INOVA-300WB spectrometer at the following settings: spectrometer frequency, 116.567 MHz; spectral width, 10 kHz; 4096 data points; 15.0-s recycle delay; 1 transients per spectrum; 128 spectra were recorded with a pulse width increment of 5 μs (spectral width, 100 kHz). The two-dimensional data sets were processed with 200-Hz and 2000-Hz line broadening in the F2 and F1 dimensions, respectively.
RESULTS

Computational Studies

As discussed by Sandi et al.[8], the average reversible capacities obtained from the different carbon precursors are very similar within the limits of the standard deviation, but pyrene exhibited the lowest irreversible capacity and capacity fade. Overall, the performance of these cells in terms of delivered capacity is significantly higher than graphite (855 mAh/g compared to 370 mAh/g at 200-300 mV vs. Li) and some other alternative materials currently under study. While some hysteresis occurs in the discharge-charge voltage profiles, these carbon electrodes deliver very high and stable capacities (>50 cycles).

The electronic energies at 0 K, $E^0_e$, were calculated for the molecular species shown in Table I. These are results from the geometry optimizations which are gas phase calculations. The calculated $\Delta E^0_e$ shown in Table II represents the difference in energy between the product and reactants at 0 K. A Mulliken population analysis was used to determine the atomic charge distributions in the molecules. The results of the geometry optimization for the $C_{60}$ carbon lattice show that there are two different carbon-carbon bond lengths within the lattice. One carbon-carbon bond length is 1.45 Å and the other is 1.37 Å. The carbon-carbon-carbon bond angles are either 120.0° or 108.0°. There are two triply degenerate lowest unoccupied molecular orbitals (LUMO’s) at -0.63eV and +1.06eV. The negative value at -0.63eV implies overlap of the LUMO with the Fermi level and therefore, perhaps, metallic conduction behavior. This may also imply ease of reduction when compared to other carbon lattice systems. For example, the geometry optimization of coronene [$C_{24}H_{12}$] using RHF/3-21G shows two doubly degenerate LUMO’s at +1.83 eV.

Structures for the two lithium-endrohedral $C_{60}$ complexes are shown in Figures 1 and 2. The $Li_2-C_{60}$ complex was initially formed by inserting a dilithium cluster with a total charge of 0 and multiplicity of 1 (paired electrons) inside $C_{60}$. The initial lithium-lithium distance for the dilithium cluster was 2.82 Å.

The distance between the two lithiums in the geometry optimized $Li_2-C_{60}$ complex is 2.96 Å. Typical lithium ion-carbon lattice bond distances vary from 2.09 to 2.55 Å for the $Li_2-C_{60}$ complex. There is very little disruption of the $C_{60}$ lattice as some bonds may increase by 0.01 to 0.05 Å due to lithium intercalation. Carbon-carbon-carbon bond angles of 120° are reduced less than 3°. Table II shows the calculated energy difference at 0 K to be -16.2 kcal/mole. This suggests a thermodynamically stable product.

Table I. Calculated Electronic Energies at 0 K for $C_{60}$ and the Endohedral Lithium Complexes of $C_{60}$.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Method Basis Set</th>
<th>Charge, Multiplicity</th>
<th>$E^0_e$ (Hartrees)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$</td>
<td>RHF/3-21G</td>
<td>0,1</td>
<td>-2259.05</td>
</tr>
<tr>
<td>$Li_2$ Cluster</td>
<td>UHF/3-21G</td>
<td>0,1</td>
<td>-14.77</td>
</tr>
<tr>
<td>Li atom</td>
<td>UHF/3-21G</td>
<td>0,2</td>
<td>-7.38</td>
</tr>
<tr>
<td>$[Li_2 - C_{60}]$</td>
<td>UHF/3-21G</td>
<td>0,1</td>
<td>-2273.85</td>
</tr>
<tr>
<td>$[Li_3 - C_{60}]$</td>
<td>RROHF/3-21G</td>
<td>0,4</td>
<td>-2281.27</td>
</tr>
</tbody>
</table>

* 1 Hartree = 627.51 kcal/mole
Table II. Calculated $\Delta E^\circ$ for Endohedral Lithium – $C_{60}$ Complexes.

<table>
<thead>
<tr>
<th>$\Delta E^\circ$ kcal/mole</th>
<th>Li-Li separation Å</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$<em>2$ Cluster + $C</em>{60}$ ↔ [Li$<em>2$ - $C</em>{60}$]</td>
<td>-16.2</td>
<td>2.96</td>
</tr>
<tr>
<td>3Li$^0$ + $C_{60}$ ↔ [Li$<em>3$ - $C</em>{60}$]</td>
<td>-47.9</td>
<td>2.60, 2.59, 2.74</td>
</tr>
</tbody>
</table>

The Li$_3$-$C_{60}$ complex was initially formed by inserting three lithiums inside $C_{60}$. After geometry optimization, it can be seen from Figure 2 that the lithiums form a triangle within the $C_{60}$ complex. As shown in Table II, the lithium-lithium distances vary from 2.59 to 2.74 Å. This is much less than that found for the spacing between lithiums in a stage 1 lithium intercalated graphite anode and is consistent with the spacing required for high capacity carbon anodes. There is very little distortion of the carbon $C_{60}$ lattice in the Li$_3$-$C_{60}$ complex. There is one notable difference, however, between the two lithium complexes. The dilithium complex appears to be ionic whereas for the trilithium complex an electron is shared between the three lithium ions. Each of the lithium ions in the trilithium complex has a value of about 0.3 for the total atomic spin density, which implies covalent bonding.

$^7$Li NMR Studies

Figure 3 is a radial concentration profile (a one-dimensional image) of the solvated Li$^+$ ions in the electrochemical cell prior to charging the cell. Each data point represents the integrated intensity of the lithium resonance in the high-resolution NMR spectrum recorded at that radial position. The spatial resolution is greatest next to the copper/carbon interface, and decreases in the...
region of the bulk electrolyte, near the counter-electrode helix. The presence of the metal helix distorts the $B_1$ field direction and magnitude to varying degrees in the region between 1.5 and 5.5 mm. This region is occupied by the bulk electrolyte and is included to clarify the spatial relationship between the one-dimensional image and the cross section of the electrochemical cell. The profile was normalized to the integral of the resonance recorded at 1.2 mm, which was assigned a lithium ion concentration of 1.0 M, *vide supra*. It appears that the Li$^+$ ion concentration in the carbon material adjacent to the bulk electrolyte is higher than in the bulk electrolyte itself. This seems highly unusual since the electrolyte in the carbon material and in the bulk should exchange readily. Perhaps the close proximity of the lithium ions to the carbon conductor enhances the NMR sensitivity, as has been observed for water on copper surfaces [9]. Near the copper electrode there is a 0.25 mm zone depleted of lithium ions. The spatial transition is quite abrupt, but the concentration profile directly adjacent to the copper conductor is not clear because the signal-to-noise ratio decreases rapidly in that region. The lithium ion concentration profile was measured again after 7.12 C of charge was passed through the cell, lithiating the carbon cathode to a theoretical C:Li ratio of 11.3:1.0, and revealed very little change. Although the $^7$Li- NMR spectrum and concentration profile were nearly identical before and after charging, the spin-lattice relaxation time constants differed by a factor of 3.64. The shorter value ($T_1 = 0.65 \pm 0.01$ s) was measured after the cell was charged and resulted from radical ion byproducts from oxidation reactions that occurred at the counter electrode.

The carbon NMR data provide details about lithium on the carbon surface, but there is not enough evidence to describe the lithium ion intercalation in the carbon lattice itself. It is our goal to incorporate a Li reference electrode in the electrochemical cell to achieve better control of the applied potential and also to provide an additional source of Li$^+$. The spatial distribution and bonding of Li in the disordered carbon lattice can then be more precisely correlated with the simulated Li$_n$-C$_{60}$ complexes.

![Figure 3: Radial concentration profile of the solvated Li$^+$ ions in the electrochemical cell.](image)

**CONCLUSIONS**

It appears as though a curved carbon lattice with low energy LUMO's can be important for lithium cluster formation as reflected by the very short lithium-lithium bond distances. This may account for the very high lithium capacities in carbon anodes. Preliminary lithium ion radial concentration profiles reveal some unusual characteristics of solvated lithium ions adsorbed into the
carbon material of the cathode in an electrochemical cell. The corresponding concentration profiles for the electrolyte solvent will be measured in order to clarify the lithium results and provide a direct measure of solvent distribution in the cathode. We plan to increase the surface area of the cathode in order to measure \textit{in situ} wide line $^7\text{Li}$ NMR spectra \cite{10} and spatial distributions of intercalated lithium ions in an electrochemical cell at various stages of the charge/discharge cycle.

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