

Lithium Diffusion in Graphitic Carbon:

Supporting Information

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Experimental setup

Both compartments “A” and “B” as described in Figure 1 were filled with 1.2 M lithium hexafluorophosphate in ethylene carbonate and ethyl methyl carbonate (1.2 M LiPF₆ in 1:2 EC:EMC) electrolyte (Ferro Corporation) and controlled by a bi-potentiostat (Astrol Electronics AG, Oberrohrdorf, Switzerland). Cell assembly and electrochemical measurement took place at room temperature (23 °C) inside a glove compartment in He atmosphere (Nexus II, Vacuum Atmospheres Company). Water and oxygen content were below 1 ppm. Prior to electrochemical tests the electrodes were dried at 120 °C under vacuum for 3 days and then transferred to the glove box without exposure to air. The diffusion experiments were repeated with HOPG membranes of different thicknesses (*i.e.*, 10, 20 and 60 μm thick). The current-time data recorded at the HOPG/electrolyte interface on compartment B was used in conjunction with the diffusion model to estimate both the diffusion coefficient of lithium in carbon as well as the concentration of lithium on the electrolyte/HOPG interface in compartment A.

Diffusion Equations

Lithium-ion transport and intercalation in highly ordered pyrolytic graphite (HOPG) membrane can be mathematically described by Fick's law under the appropriate initial and boundary conditions given for the experimental setup:

$$\frac{\partial C_{Li^+}}{\partial t} = D_{Li^+} \frac{\partial^2 C_{Li^+}}{\partial x^2} \quad 1$$

$$C_{Li^+} = 0 \text{ for } 0 \leq x \leq L \text{ and } t = 0 \quad 2$$

$$C_{Li^+} = C_{Li^+}^0 \text{ for } x = 0 \text{ and } t \geq 0 \quad 3$$

$$C_{Li^+} = 0 \text{ for } x = L \text{ and } t \geq 0 \quad 4$$

where C_{Li^+} is the Li concentration as a function of time and position in the HOPG membrane, D_{Li^+} is the diffusion coefficient, $C_{Li^+}^0$ is the concentration of Li at the HOPG/electrolyte interface in compartment A. For a given experiment (*i.e.*, lithium diffusion through edge-plane or basal-plane), only one diffusion coefficient was used to fit the data. Though two different modes of diffusion are possible (*i.e.*, along the grain boundaries as well as along the graphene planes) for each of the experiments performed, transport in only one direction (*i.e.*, 1-D) was considered in this model. This is because diffusion in only one direction was dominant or limiting in each of the two kinds of experiments performed – *i.e.*, diffusion through the grain-boundaries was limiting in the basal-plane experiment and diffusion along the graphene layers was significantly faster in the edge-plane experiment.

The steady-state limiting current is given by Eq. (4)

$$i(t) = n_e F A D_{Li^+} \left. \frac{\partial C_{Li}}{\partial x} \right|_{x=L} \quad 5$$

where n_e is the number of electrons in the electrochemical reaction of interest (here one), F is Faraday's constant and A is the cross-sectional area of the working electrode. The response current $i(t)$ measured at $x = L$ was fit to Eq. 5.

The method of least squares¹ was used to fit the data from each trial to Eq. 5 and solve for the diffusion coefficient and lithium concentration at the HOPG/electrolyte interface in compartment A simultaneously. To determine the accuracy of values obtained for D_{Li^+} and $C_{Li^+}^0$, confidence intervals were obtained by using the method described by Kimble and White² shown in Eq. 6,

$$P_k = \hat{P}_k \pm t_\gamma s_{\hat{P}_k} \sqrt{C_{kk}} \quad 6$$

where \hat{P}_k is the estimate of parameter P_k found through the least squares method, $s_{\hat{P}_k}$ is the standard deviation for the data set, and t_γ is the value of the t-distribution (also known as the student distribution)^{3,4} with a confidence, γ . Eq. 7 is solved for t_γ to obtain the t-distribution,

$$\int_{t_\gamma}^{\infty} \frac{\Gamma[(f-1)/2]}{\sqrt{\pi f} \Gamma(f/2)} \left(1 + \frac{x^2}{f}\right)^{-\frac{f+1}{2}} dx = \alpha \quad 7$$

$$\alpha = (1 - \gamma)/2 \quad 8$$

where f is the degrees of freedom and is equal to $(n - m)$, where n is the number of data points and m is the number of parameters (two in this case, D_g and c_g).

A value for C_{kk} in Eq. 6 can be obtained from the approximate Hessian Matrix,

$$N = \begin{bmatrix} 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_{D_g}} \frac{\partial i(j)}{\partial P_{D_g}} & 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_{D_g}} \frac{\partial i(j)}{\partial P_{c_g}} \\ 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_{c_g}} \frac{\partial i(j)}{\partial P_{D_g}} & 2 \sum_{j=1}^n \frac{\partial i(j)}{\partial P_{c_g}} \frac{\partial i(j)}{\partial P_{c_g}} \end{bmatrix} \quad 9$$

where $i(j)$ is the current, i , recorded at each data point, j . Equation 9 is then inverted and the diagonal elements of that matrix, $N[1,1]$ and $N[2,2]$, are taken as C_{kk} ($C_{D_g D_g}$ for diffusivity and $C_{c_g c_g}$ for lithium concentration at the HOPG/electrolyte interface in compartment A).

First Principles Calculations

The binding force between the graphene sheets in graphite originates from inter-layer van der Waals (vdW) interactions, which are not accurately captured in standard DFT.⁵ Thus, in GGA, the

binding force between the graphene sheets is negligible and the interlayer distance for empty graphene-graphene layers needs to be fixed to the experimental value of 6.70 Å.⁶ However, at moderate and high intra-layer lithium concentrations the Li–C interactions, which are well described within the DFT framework, dominate over the vdW forces. Thus, for lithium-containing layers, the inter-layer distance is well re-produced. It has been argued that the local density approximation (LDA) spuriously mimics a fraction of the vdW interaction (see Ref. 7 and references therein), which would improve the treatment in graphite and the low lithium concentration part of the phase diagram. However, LDA also severely overestimates the Li–C binding⁸, which affects not only phase stability but also Li migration barriers. This is evident when comparing the migration barriers obtained in Ref [13] to our corresponding ones. Because we are more interested in obtaining the correct order of magnitude for the Li – C binding energies – especially in the non-dilute lithium concentration regime - we have chosen to use the GGA.

Stage I and stage II Li–graphite phases were explored, which covers a broad part of the Li-graphite phase diagram. We calculated the energies of 63 different Li-vacancy arrangements in stage I and stage II forms of Li_xC_6 . For stage I, both the graphite and Li layers had an *AA* stacking sequence⁹ while in stage II, non-Li containing graphite layers had an *AB* stacking sequence. Two separate cluster expansions for stage I and stage II were employed to model partially disordered states at finite temperatures.¹⁰⁻¹² This choice of clusters for the stage I (stage II) cluster expansions resulted in a weighted cross validation score of 22.4 meV/6C (4.6 meV/6C) and an RMS error of 8.8 meV/6C (2.5 meV/6C). The Li ordering of the first-principles calculated ground states matched the ground states obtained in the cluster expansions.

Kinetic Monte Carlo simulations were employed to calculate Li diffusion coefficients as a function of Li concentration in stage I and stage II compounds. The chemical diffusion coefficient D_C , which determines macroscopic diffusion as defined by Fick’s law, can be factored according to

$$D_C = \Theta D_J \quad 10$$

where Θ is the thermodynamic factor, $\Theta = [\partial(\mu/k_B T) / \partial \ln x]$ and D_J is the jump diffusion coefficient

$$D_J = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \left\langle \frac{1}{N} \left(\sum_{i=1}^N \vec{r}_i(t) \right)^2 \right\rangle \right] \quad 11$$

In Eq. 11, \vec{r}_i denotes the displacement of i^{th} lithium ion after time t , N corresponds to the number of diffusing Li ions and d is the dimension of the network that the diffusion occurs on ($d = 2$ for graphite). The jump diffusion coefficient is frequently approximated, as in the case of this work, by the tracer-diffusion coefficient,

$$D^* = \lim_{t \rightarrow \infty} \left[\frac{1}{2dt} \left\langle \frac{1}{N} \sum_{i=1}^N \left[\dot{\vec{r}}_i(t) \right]^2 \right\rangle \right] \quad 12$$

which neglects cross correlations between displacements of different particles. The trajectories $\dot{\vec{r}}_i(t)$ can be calculated in kinetic Monte Carlo simulations provided an accurate description of elementary hop events is available. We can approximate the frequency with which Li ions move to vacant neighboring sites with transition state theory according to:

$$\Gamma = \nu^* \exp(-\Delta E_h / k_B T) \quad 13$$

where ΔE_h is the difference between the energy at an activated state and the initial equilibrium state and ν^* is an effective vibrational frequency, here taken as $1 \times 10^{13} \text{ s}^{-1}$, which is carefully calculated in Ref. 13 from first principles. The kinetic Monte Carlo simulations were performed using a direction-independent barrier model.¹⁴ The DFT calculations of migration barriers were performed in super cells where the hopping ions were at least 7 \AA apart in-plane and at least one non-hopping Li layer or empty layer between every layer with hopping ions. The location and energy of the activated states were determined by the nudged elastic band method,¹⁵ as implemented in VASP. For stage II we obtained a

Li migration barrier of 297 meV, while for stage I, the barrier obtained was 283 meV. The diffusion coefficients were obtained through kinetic Monte Carlo simulations in 12x12x12 cells over a fixed temperature of 300 K using 1000 sampling passes with 500 equilibrium passes and 50-100 ensemble averages.

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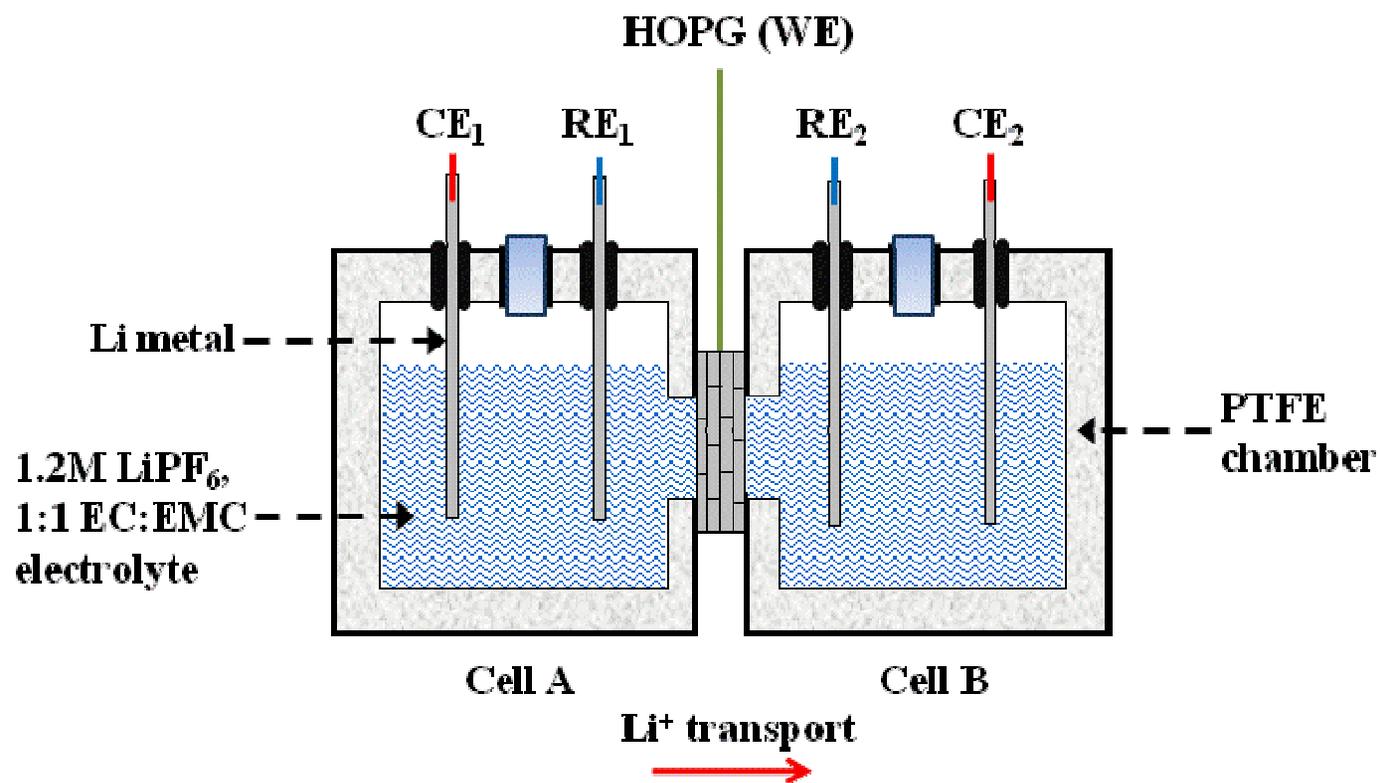


Figure 1: Schematic of the Devanathan-Stachurski type diffusion cell used in this study for measuring lithium-transport properties in HOPG. The HOPG membrane served as a common working electrode (WE) for both cells. Lithium metal served as counter (CE) and reference electrodes (RE) for both cells.