A new battery-charging method suggested by molecular dynamics simulations

Ibrahim Abou Hamad\textsuperscript{1,}\textsuperscript{*}, M. A. Novotny\textsuperscript{1,2}, D. Wipf\textsuperscript{3}, and P. A. Rikvold\textsuperscript{4}

\textsuperscript{1}HPC\textsuperscript{2}, Center for Computational Sciences, Mississippi State University, Mississippi State, Mississippi 39762
\textsuperscript{2}Department of Physics & Astronomy, Mississippi State University, Mississippi State, Mississippi 39762
\textsuperscript{3}Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762
\textsuperscript{4}Department of Physics and Center for Materials Research and Technology
Florida State University, Tallahassee, Florida 32306-4350

March 9, 2010

Abstract

Based on large-scale molecular dynamics simulations, we propose a new charging method that should be capable of charging a Lithium-ion battery in a fraction of the time needed when using traditional methods. This charging method uses an additional applied oscillatory electric field. Our simulation results show that this charging method offers a great reduction in the average intercalation time for Li\textsuperscript{+} ions, which dominates the charging time. The oscillating field not only increases the diffusion rate of Li\textsuperscript{+} ions in the electrolyte but, more importantly, also enhances intercalation by lowering the corresponding overall energy barrier.

1 Introduction

The widespread use of Lithium batteries with liquid electrolytes in portable electronics, as well as their potential for use in environmentally friendly electric vehicles, make

\textsuperscript{*}Current address: Department of Physics and Center for Materials Research and Technology, Florida State University, Tallahassee, FL 32306-4350, USA, E-mail address: iabouhamad@fsu.edu
At the same time, revolutionary developments in computer hardware and algorithms now enable simulations with millions of individual particles. Computer simulations, ranging from molecular dynamics (MD) to Monte Carlo (MC) simulations and quantum-mechanical density functional theory are therefore becoming widely used to model electrochemical systems and guide experimental research. Quantum-mechanical simulations have been used to study the average voltage needed, the charge transfer, and the phase diagrams for Lithium intercalation in transition metal oxides. Studies of a graphite electrode with intercalated Lithium and of surface chemistry at the electrode-electrolyte interface have also used quantum-mechanical simulations. MD and MC simulations have contributed important insight about the interfacial structure, structural changes and Lithium ion diffusion in Lithium batteries in the anode or cathode half cell. These studies were all performed under stationary voltage conditions.

The Lithium-ion battery-charging process is marked by the intercalation of Lithium ions into the anode material. Here we present large-scale molecular dynamics simulations of this process under oscillating voltage conditions. These simulations suggest a new charging method that has the potential to deliver much shorter charging times, as well as the possibility of providing higher power densities. Moreover, it is argued that while the chemical nature of the electrodes decides the energy output, the electrolyte, in most situations, controls the rate of mass flow of the ions and thus how fast energy can be stored or released. Our simulations suggest that while faster diffusion contributes to faster charging, the rate-limiting step is the Li-ion intercalation into the graphite anode.

The rest of this paper is organized as follows. The details of the molecular-dynamics simulations, as well as the composition of the model system are presented in section 2. The simulation results and a discussion of diffusion and intercalation times are presented in section 3. The paper ends with a conclusions section.
2 Model and simulation method

The model system for the anode half-cell of a Lithium-ion battery is composed of an anode represented by a stack of graphite sheets, an electrolyte of ethylene carbonate and propylene carbonate molecules, and Lithium and hexafluorophosphate ions. After reaching a constant volume with simulations in the NPT ensemble, long production runs are done in the NVT ensemble at room temperature.

2.1 Molecular Dynamics

Molecular Dynamics is based on the solution of the classical equations of motion for a system of \( N \) interacting atoms. From the potential energy \( E_P \), the instantaneous force, acceleration, and velocity for the \( i \)th atom are calculated, and its position is updated accordingly. This process is repeated for all atoms at each time step.

The General Amber Force Field (GAFF) was used to approximate the bonded and van der Waals’ interactions of all the simulation atoms, while the simulation package Spartan (Wave-function, Inc., Irvine, CA) was used at the Hartree-Fock/6-31g* level to obtain the necessary point charges for the ethylene carbonate, propylene carbonate and \( \text{PF}_6^- \). The charges were slightly modified to make the charges equal on identical atoms while keeping the sum of the charges constant. The AMBER program *tLeap* was used to build the molecules and set their force field parameters and combine them into one parameter input file for the system as a whole. The simulation package NAMD was used for the MD simulations, while VMD was used for visualization and analysis of the system. NAMD was primarily chosen because it is a parallel MD program that scales remarkably well with the number of processors.

2.2 Model System

The anode half-cell is modeled using four graphite sheets containing 160 carbon atoms each (anode), two \( \text{PF}_6^- \) ions, and ten \( \text{Li}^+ \) ions, solvated in an electrolyte composed of 69 propylene carbonate and 87 ethylene carbonate molecules (see Fig. 1). The anode sheets were fixed from the side by keeping the positions of the carbon atoms at one
The system was first simulated in the NPT ensemble until it reached constant volume. The system has periodic boundary conditions and is simulated at one atm and 300 K. Top view, perpendicular to the plane of the graphite sheets (a) Snapshot after 200 ns MD simulation in the NVT ensemble of the model system containing four graphite sheets, two PF$_6^−$ ions and ten Li$^+$ ions, solvated in 69 propylene carbonate and 87 ethylene carbonate molecules. (b) Snapshot after 19 ns MD simulation with an additional oscillating electric field. The charges on the carbon atoms of the graphite sheets was set to −0.0125 e per atom to simulate a charging field.

The simulations proceeded as follows. The system energy was minimized, after which the simulations were run at constant pressure (in the NPT ensemble) using a Langevin piston Nosé-Hoover method$^{21,22}$ as implemented in the NAMD software package until the system had reached its equilibrium volume at a pressure of 1 atm and 300 K. The system’s behavior was then simulated for 200 ns (100 million steps) in the NVT ensemble. A 2 fs timestep was used. The electrostatic interactions were calculated by the particle-mesh Ewald method$^{23,24}$.

The Li$^+$ ions stay randomly distributed within the electrolyte, and none of the Li$^+$ ions intercalates between the graphite sheets after 200 ns (see Fig. 1(a)). This behavior was confirmed by 10 independent runs. While it is expected that, given sufficient time, the Li$^+$ ions would move closer to the electrode and intercalate between the graphite sheets, they do not show such behavior on the time scales currently accessible by molecular dynamics simulations.

For intercalation to occur, the Lithium ion has first to diffuse within the electrolyte
until it reaches the graphite electrode, and second to overcome the energy barrier at the electrode-electrolyte interface. In order to facilitate intercalation, a new charging method was explored. An external oscillating square-wave field (amplitude \( A = 5 \) kCal/mol, frequency \( f = 25 \) GHz) was applied in the direction perpendicular to the plane of the graphite sheets. This oscillating field is in addition to the charging field due to the fixed charge on the graphite carbons. This additional field not only increases diffusion, but also causes some of the Lithium ions to intercalate into the graphite sheets within an average time of about 50 ns for the amplitude and frequency mentioned above, calculated from 100 independent runs.

### 3 Simulation Results

The simulations were performed on 2.6 GHz Opteron processors, using 160 processors at a time. The amplitude of the oscillating field was fixed at values from 0.9A to 1.3A in steps of 0.1. For each value of the amplitude ten simulations were collected. For the value of the amplitude equal to \( A \), 100 different runs were simulated. The total computer time required was approximately \( 4 \times 10^5 \) CPU hours. The data were used to study the dependence of the diffusion and intercalation times on the field amplitude. A study of this dependence on the field frequency is currently initiated.

#### 3.1 Diffusion

The use of the additional oscillating field leads to much faster diffusion. Figure 2 shows the average root-mean-square displacement of the Li\(^+\) ions as a function of time. The average is over all the ten Li\(^+\) ions and over the number of different simulations for each value of the amplitude of the electric field. When using an oscillating electric field, within the first 2 ns of simulation the root-mean-square displacement reaches a value close to its limiting value defined by the finite size of the system, while much slower diffusion is seen for the simulations without that additional field. The inset shows a comparison of the root-mean-square displacement for a single run with and without the oscillating electric field of frequency 25 GHz and amplitude \( A \) for a much
Figure 2: Average root-mean-square displacement of Lithium ions as a function of time. Diffusion is much faster with the additional oscillating field with frequency 25 GHz for all values of its amplitude ($\times A$ with $A = 5$ kCal/mol). A comparison between two long simulation runs with and without the oscillating field is shown in the inset. Notice that the lower curve (without oscillating field) only approaches the upper curve (with oscillating field) after about 100 ns of simulation time.

longer time period. The root-mean-square displacement for simulations without the oscillating electric field start approaching the limiting value only after about 100 ns of simulation time. The diffusion coefficient estimated from the root-mean-square displacement of Li ions in the electrolyte, from simulations without an oscillating electric field, is about $4 \times 10^{-12} \text{ m}^2/\text{s}$, which is consistent with the results from a different MD study by Márquez\cite{Márquez}.

### 3.2 Intercalation time

The inclusion of an additional oscillating electric field not only increases the diffusion rate, but also leads to the intercalation of Lithium between the graphite sheets. The intercalation events of the Lithium ions are considered to be a Poisson process.\cite{Márquez} Then the fraction of the number of runs simulated, in which no ions have intercalated by time $t$, is given by

$$P_{\text{non}} = e^{-t/\tau},$$

(1)

where $\tau$ is the average intercalation time for that process. Thus, the average intercalation time can be obtained from a fit of the fraction of non-intercalated ions as a function
Figure 3: Fraction of non-intercalated Lithium ions versus time. The lines are fits to the form given by Eq. (1), and the fitted parameters are shown in the legend for the different amplitudes of the applied oscillating field. The denominator in the exponential is the average intercalation time in ns.

of time to the form given by equation 1. A plot of the fraction of non-intercalated ions versus time, as well as the fitting lines and average intercalation times are shown in Fig. 3. The frequency used was always 25 GHz. The standard deviation is assumed to be on the order of $\sigma$, and the error bars on the fitting parameters are calculated using a $1/\sigma^2$ weighted linear-regression analysis (Fig. 4).

The dependence of the average intercalation time on the amplitude of the applied oscillating electric field is shown in Fig. 4. The average intercalation time shows an exponential dependence on the amplitude of the applied field. This dependence is consistent with a linear decrease of the effective free-energy barrier against intercalation with increasing amplitude of the applied field. However, due to the small window of amplitude values, other forms of the dependence of the barrier on the field amplitude cannot be excluded. Moreover, care must be taken in extrapolating this dependence outside of the simulated amplitude range. Extrapolating to a large amplitude of about
2.78 Å, the time would be equal to the MD time step. In the more interesting regime of small amplitudes, extrapolating to zero amplitude would lead to an average intercalation time of $6.7 \times 10^5$ ns. This time scale is clearly larger than the maximum time for which MD simulations of a system of this complexity can presently be performed. For no oscillatory field, as in Fig. 1(a), we performed simulations for a total time of about 200 ns without observing any intercalations. These simulations were performed with a uniform charge distribution on the C atoms. Since graphite is a conductor, it is likely that the charge distribution is biased toward the electrode surface. To check the influence of the charge distribution, we therefore performed exploratory simulations with the electronic charge distributed over just the two C layers near the interface. In these simulations (Amplitude 1.3 Å) we found only an insignificant change in the diffusion time, while the intercalation time increased by approximately a factor of three. However, this is still very much shorter than the constant-field case. Thus, the qualitative effect of the oscillating field is independent of the details of the charge distribution.

The charging time in our simulations depends exponentially on the amplitude of the oscillating field, while diffusion did not differ much for different values of the amplitude (see Fig. 2). Included in the intercalation times are the time to diffuse toward
the electrode and the time to overcome the electrode-electrolyte interface barrier. This leads us to two conclusions. First, the oscillating field not only increases the diffusion rate, but it also lowers the free-energy barrier for intercalation. Second, while diffusion is important for faster charging, the rate-limiting step for our case is the intercalation process.

4 Conclusions

In this paper we have proposed a new charging method for Lithium-ion batteries that uses an additional oscillating electric field to reduce the average intercalation time, and thus the charging time. The dependence of the intercalation time on the applied field amplitude is exponential, and thus there is the potential for very fast charging times.

This exponential dependence indicates that while the oscillating field does increase the diffusion rate of Li$^+$ ions (not exponentially), more importantly it enhances intercalation through lowering the intercalation free-energy barrier. While faster diffusion is important for faster charging, lowering the intercalation barrier at the electrode-electrolyte interface is seen to be more important in the frequency and amplitude regimes we were able to simulate using molecular dynamics simulations. Future work will consider the effect of different frequencies, as well as quantitative comparison with electrochemical experiments where possible.

Acknowledgements

This work was supported by U.S. National Science Foundation Grant No. DMR-0802288 (Florida State University) and by the HPC$^2$ Center for Computational Sciences (Mississippi State University).

References

[1] M. Armand and J. M. Tarascon, Nature, 2008, 451, 652–657.
[2] K. Xu, *Chemical Reviews*, 2004, **104**, 4303–4418.

[3] P. Vashishta, R. Kalia and A. Nakano, *J. Phys. Chem. B*, 2006, **110**, 3727–3733.

[4] P. A. Rikvold, I. Abou Hamad, T. Juwono, D. T. Robb and M. A. Novotny, in *Modern Aspects of Electrochemistry*, ed. M. Schlesinger, Springer-Verlag, Berlin Heidelberg, 2009, vol. 44, ch. 4, pp. 131–149.

[5] M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho and J. Joannopoulos, *Phys. Rev. B*, 1997, **56**, 1354–1365.

[6] G. Ceder and A. V. der Ven, *Electrochim. Acta*, 1999, **45**, 131 – 150.

[7] A. Márquez, A. Vargas and P. B. Balbuena, *J. Electrochem. Soc.*, 1998, **145**, 3328–3334.

[8] Y. Wang, S. Nakamura, K. Tasaki and P. B. Balbuena, *J. AM. Chem. Soc.*, 2002, **124**, 4408–4421.

[9] R. Darling and J. Newman, *J. Electrochem. Soc.*, 1999, **146**, 3765–3772.

[10] A. Márquez, *Mater. Chem. Phys.*, 2007, **104**, 199 – 209.

[11] A. Márquez and P. B. Balbuena, *J. Electrochem. Soc.*, 2001, **148**, A624–A635.

[12] M. E. Garcia, E. W. III and S. H. Garofalini, *J. Electrochem. Soc.*, 1998, **145**, 2155–2164.

[13] M. E. Garcia and S. H. Garofalini, *J. Electrochem. Soc.*, 1999, **146**, 840–849.

[14] *Handbook of Batteries*, ed. D. Linden, McGraw-Hill, New York, 3rd edn., 2001.

[15] M. P. Allen and D. J. Tildesly, *Computer Simulation of Liquids*, Claredon Press, Oxford, 1992.

[16] J. M. Haile, *Molecular Dynamics Simulation, Elementary Methods*, John Wiley & Sons, New York, 1992.

[17] D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, Cambridge University Press, Cambridge, 2nd edn., 2004.
[18] J. Wang, R. Wolf, J. Caldwell, P. Kollman and D. Case, J. Comp. Chem., 2004, 25, 1157.

[19] J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kalé and K. Schulten, J. Comp. Chem., 2005, 26, 1781–1802.

[20] A. D. W. Humphrey and K. Schulten, J. Mol. Graphics, 1996, 14, 33–38.

[21] G. J. Martyna, D. J. Tobias and M. L. Klein, J. Chem. Phys., 1994, 101, 4177–4189.

[22] S. E. Feller, Y. Zhang, R. W. Pastor and B. R. Brooks, J. Chem. Phys., 1995, 103, 4613–4621.

[23] T. Darden, D. York and L. Pedersen, J. Chem. Phys., 1993, 98, 10089.

[24] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee and L. G. Pedersen, J. Chem. Phys., 1995, 103, 8577.

[25] I. Abou Hamad, M. A. Novotny and P. A. Rikvold, in preparation.

[26] D. R. Cox and H. D. Miller, The Theory of Stochastic Processes, Wiley publications in statistics, New York, 1965.