Molecular Dynamics simulations to uncover the mechanism of hydrogen retention in lithiated graphite

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1. Introduction

- Lithiated graphite material as the first wall in future fusion reactor may suppress or even eliminate problems of *tritium retention* and *surface erosion* [1]
- However, the mechanism of hydrogen bonding with lithiated graphite is unknown and this study seeks to elucidate on this mystery.
- Molecular Dynamic (MD) simulation helps to understand the behavior of lithium-carbon mixed materials from atomic level
- Li, C, O and H are of very different electronegativities and therefore the system could be considered as ionic solids. This implies it is important to model the polarization which is usually avoided in MD simulations due to possible computational cost.
- We studied the system dynamics (e.g. hydrogen retention and sputtering) via two approaches: Quantum-Classical Molecular Dynamics (QCMD) and Classical Molecular Dynamics (CMD).
- For the quantum-mechanical part of the approach we employed Self Consistent Charge Density Functional Tight Binding (SCC-DFTB) method [2], developed by the Bremen (Germany) Center for Computational Material Sciences. We adapted it for the trajectory Monte Carlo calculation on the parallel computers.
- For the CMD part, a new multi-body potential is in development for this mixed material based on Tersoff-Brenner type of bond-order potential [3] and the electronegativity equalization method (EEM)[4] for calculation of charge distribution.

2. Theory and Methods

1. The experimental basis

- The experimental results by Allain and Taylor [5] indicate that Li-C/O sites are preferred by retained H. Also, recent results showed there is no energy dependence for this functionality (Fig 1), which is an important basis for the simulations, since different energies than experiments were used in the MD simulations to try to prove the experimental hypothesis.

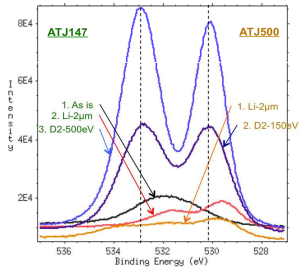


Fig 1. Oxygen 1s peaks

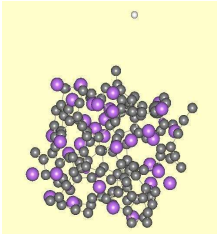


Fig 2. Structure of a typical simulation cell; Black (carbon), violet (lithium) and white (hydrogen).[7]

2. SCC-DFTB

- The pair-parameters for the Li-C-O-H system is provided by K. Morokuma and S. Maeda [6].
- Cell of a few hundreds of atoms of lithiated amorphous carbon (about 20% of Li) by thermalization bombarded by 2.5 eV H atoms, as shown in Fig 2. Total 5004 random trajectories were applied, with the time step of 0.2 fs. [7]

3. CMD

$$E_{bond} = \sum_{i>j} f_{ij}^{c}(r_{ij})[V_{ij}^{R} - \frac{b_{ij}+b_{ji}}{2}V_{ij}^{A}(r_{ij})]$$

Bond-order potential. Cut-off radius: 2nm. Need parameter fitting.

$$E_{tot} = E_{bond} + E_{nobond}$$

$$E_{nobond} = E_{coul} + E_{vdW}$$

Long range interactions Cut-off radius: 10 nm.

$$E_{vdW} = \sum_{i}\sum_{j>i} D_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - 2(\frac{\sigma_{ij}}{r_{ij}})^{6}]$$

Lennard-Jones potential

$$E_{coul} = \sum_{i}\sum_{j>i} \frac{q_i q_j}{r_{ij}}$$

Coulombic interaction: the dominant long-distance binding force between particles in Li-C-H system. Charges are calculated by EEM approach.

3. Results

1. QCMD

The distributions of the charges are obtained by the following approach: average charges of Li and C are calculated for the final distribution of each retained trajectory, while the H charge is recorded at the termination point of the retaining trajectory.

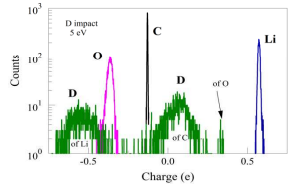


Fig 3. Charge distributions of retained D, as well as of Li, C. and O upon the retention process. [7]

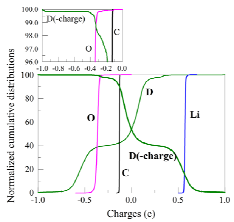


Fig 4. Normalized cumulated distributions of retained D in comparison to C, Li and O [7]

2. CMD – parameterization

2.1 Bond order potential fitting

Table 1. Parameters for the attractive and repulsive pair terms of the bond order potential

	C-Li	H-Li	Li-Li
A	-122.1392	-61.7395	-1.2242
α	2.9174	1.4796	0.4154
B	21.0963	3.1725	3.2945
β	0.829	0.6666	0.2388
Q	-6.7493	-1.321	-8.0102

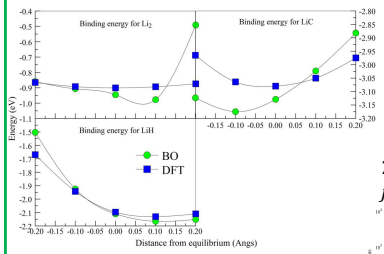


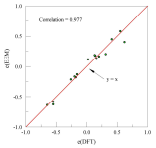
Fig 5. Comparison of the binding energies of the dimers Li2, LiH, & LiC; computed from DFT (green circles) and the results of the BO calculation (blue squares).

2.2 EEM parameters

- A semi-empirical approach to density functional theory. It allows the direct calculation of the charge distribution in a molecule or solid. The accuracy depends on the pre-determined parameters.
- In EEM, the electronegativity of an atom α in an N-atom molecule is shown to be:

$$\chi_{eq} = \chi_{\alpha} = \chi_{\alpha}^{*} + 2\eta_{\alpha}^{*}q_{\alpha} + \sum_{\beta\neq\alpha}^{N}\frac{q_{\beta}}{R_{\alpha\beta}}$$

Atom	EEM parameters	
	χ (ev)	η(ev)
C	2.63	3.14
H+	1.42	1.02
H-	1.79	0.81
Li	0.80	0.87



Above:
Table 2. The EEM parameters fitted by the training set consisting of 6 small molecules.
Fig 6. Comparison of charges calculated by DFT and EEM for these 6 small molecules

2.3. Comparison of EEM to DFTB for charge calculation

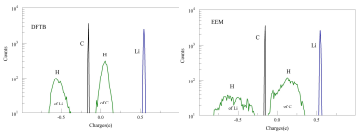


Fig 7 Charge distribution calculated by DFTB and EEM

4. Conclusions

- From the QCMD studies, the influence of Li, present at 20% of the total number of atoms in the cell, substantially changes the retaining chemistry, significantly increasing the probability of collecting the H atoms in its neighborhood, in accordance with the observation. These results have very important ramifications for our understanding of the use of lithium surface coatings and lithization strategies in magnetic fusion confinement plasmas.
- According to the comparison of the charge calculation, EEM approach has demonstrated the ability to reproduce the DFTB results well. It implies the potential application of this approach to DFTB for charge calculation to accelerate the simulation speed.
- Still, the verification of the new MD potential needs to be done by cumulative bombardment of H analysis. This is our future research plan.

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Plasma Facing Components 2011 Meeting
August 10 – August 12, 2011, Oak Ridge National Lab, Oak Ridge, TN, USA

Acknowledgements We acknowledge support of DoE and Laboratory Directed Research and Development Program of ORNL, under contract No. DE-AC05 00OR 22725 with UT-Battelle, LLC. Work is also supported by US DOE Contract DE-FG02-08ER54990, DE-AC02-09CH11466. ZCY acknowledges the ORISE/ORAU program HERE and DoE for support of his research at ORNL.