Ab-initio Calculations for a Lithium/Diquinoxalinylene Battery

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ABSTRACT : As a part of our efforts to further develop organic-based cathode active materials for high performance lithium-ion based batteries, ab-initio density functional theory calculations were performed on a 2Q (diquinoxalinylene) active material. Using Gaussian 16 software, the ground-state molecular structures and ESP (electrostatic potential) mapped density surface contours for the $2Q\text{-}Li_x$ (x = 0 to 5) molecules were determined. For a lithium/$2Q\text{-}Li_x$ cell, open-circuit cell voltages were determined at 0K for the gas phase and 298.15K for the solution phase to see the effect of temperature and solvation and to compare against experimentally measured values.

KEYWORDS: batteries, lithium, organic, computational chemistry, cathode, secondary

I. INTRODUCTION

In a recent article [1], results on the successful development and testing of two different rechargeable organic-based cathode materials based on quinoxaline are presented. A schematic of quinoxaline is shown in Figure 1 below.
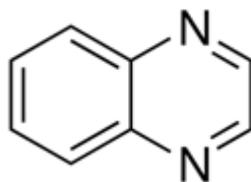

Figure 1. Schematic diagram of quinoxaline.

The two different cathode materials were diquinoxalinylene (2Q) and triquinoxalinylene (3Q) and the chemical structures, determined using Gaussian 16, are shown in Figures 2 and 3, respectively. (Note: For the chemical structures in this paper, white represents hydrogen, gray represents carbon, blue represents nitrogen, red represents oxygen, and pink represents lithium.)
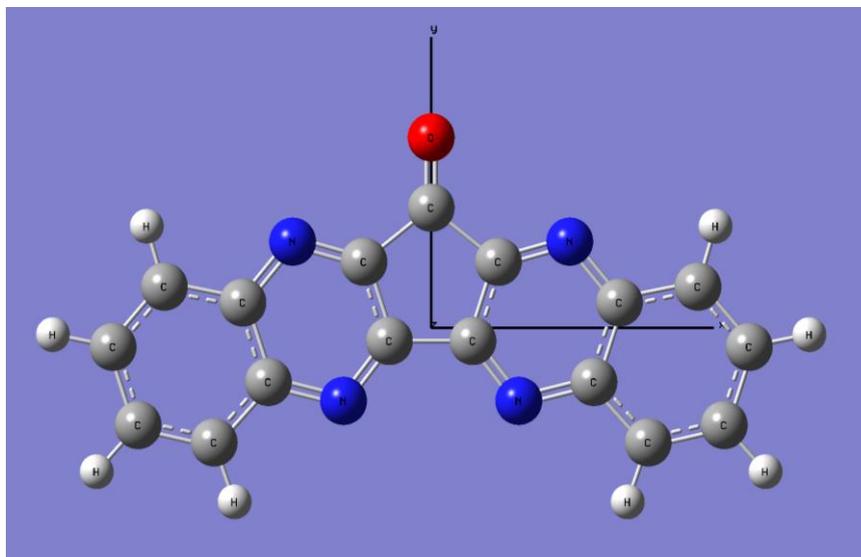

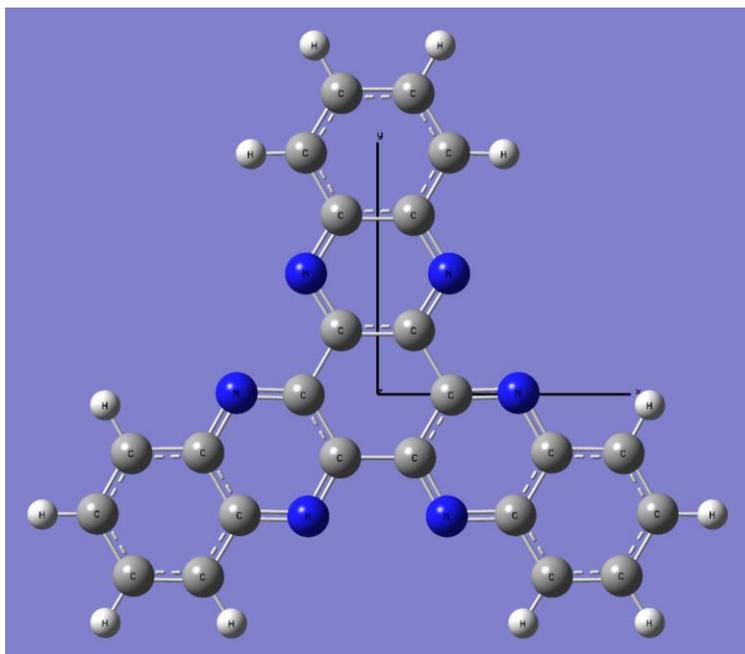Figure 2. Chemical structure of the 2Q compound.

Figure 3. Chemical structure of the 3Q compound.

Both cathode materials performed very well in terms of rate capability, capacity, and cycle life. For example, a 2016-type coin cell using the 2Q cathode active material, had reversible capacities of 373 and 222 mAh/g at the 1C and 20C discharge rates, respectively. The 2Q coin cells also demonstrated a capacity of around 185 mAh/g at the 20C discharge rate after 10,000 cycles. Lithium foil was used as the anode material, 1.0 M lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) in 1,3 dioxolane (DOL)/1,2 dimethoxyethane (DME) as the electrolyte solution, and the cathode contained 60 wt% graphene, 10 wt% PVDF binder, and 30 wt% active material. The separator material used was Whatman GF/D filter paper.

II. DENSITY FUNCTIONAL THEORY COMPUTATIONS FOR 2Q

Density functional theory (DFT) was used to computationally determine properties of the 3Q active material [1]. They used the Gaussian 09 software package with use of the B3LYP hybrid functional and the 6-31+G(d,p) basis set. Solvent effects were also simulated using the polarization continuum model (PCM) with 1, 2-dimethoxyethane (DME) as the solvent. In order to further understand the effects of the DFT methods used by the authors [1] on the cell potentials for the 2Q active material, we performed similar calculations using Gaussian 16 and hybrid functional/basis sets B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p), and B3LYP/6-31+G(d,p) with PCM solvent effects. In going from B3LYP/6-31G(d,p) to B3LYP/6-31+G(d,p), there was minimal change in the energies. Therefore, Tables 1 and 2 shows just the effects of going from B3LYP/6-31G(d,p) to B3LYP/6-31+G(d,p) with PCM using diethyl ether (DEE) as the solvent (note: DEE is similar to DME, but, was easier to implement.) There is maximum difference up to 0.47 volts in the computed cell voltage for the gas phase at 0K compared to the inclusion of the DEE solvent at room temperature for the 2Q material. Thus, there is a noticeable difference in the cell voltage calculation when one includes the effects of solvation.
Figure 4 shows the optimized ground state structures for 2Q and the electrostatic potential (ESP)-mapped electronic density. Note that near the oxygen and nitrogen atoms, the ESP map is red and it is blue by the peripheral hydrogen atoms.
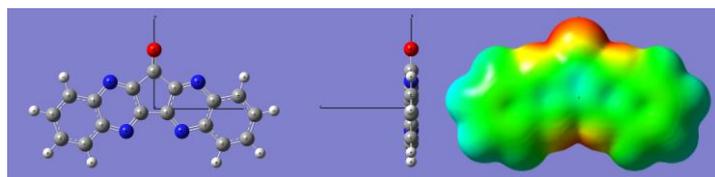

Figure 4. 2Q structure from G16 optimization and ESP-mapped electronic density.

After performing computations on one lithium atom reacting with the 2Q molecule, a ground state energy computation on having a lithium atom reacting with 2Q-Li was performed. Figure 5 shows the structural and

ESP-mapped electronic density results. Note that the molecule retains its planar structure, the lithium appears to bond with two carbon atoms and the oxygen atom, and the color for the lithium occupied region (in the ESP-mapped electronic density contour) is now blue. Figure 6 shows the computational results when a lithium atom reacts with 2Q-Li to form 2Q-Li$_2$. Note the molecule mainly retains its rigid planarity and where the new lithium ion resides has turned the ESP surface map blue. Optimizations were also performed where the lithium atom was placed near the center of one of the benzene rings and also by placing it near the nitrogen atoms opposite the oxygen atom, but the optimized ground state energy for these configurations were slightly higher than that of the configuration shown in Figure 6. Figure 7 shows the computational results when a lithium atom reacts with 2Q-Li$_2$ to form 2Q-Li$_3$. Note the molecule mainly retains its rigid planarity and where the new lithium ion resides has turned the ESP surface map blue. Optimizations were also performed where the lithium atom was placed near the center of one of the benzene rings and also by placing it near the nitrogen atoms that already have a lithium ion, but the optimized ground state energies for these configurations were slightly higher than the energy of the one shown in Figure 7.

Table 1. Calculated Free energies at 0K and 298.15K for 2Q using Gaussian 16.

Active Material	B3LYP/6-31G(d,p) Free Energy at 0K (Hartrees)	B3LYP/6-31+G(d,p) in DEE solution Free Energy at 298.15K (Hartrees)
Lithium	-7.504387	-7.517824
2Q	-946.8692612	-946.740392
2Q-Li	-954.4763662	-954.370633
2Q-Li$_2$	-962.0827927	-961.986582
2Q-Li$_3$	-969.661928	-969.580269
2Q-Li$_4$	-977.183158	-977.131309
2Q-Li$_5$	-984.6979078	(not converged)

Table 2. Calculated cell voltages at 0K and 298.15K.

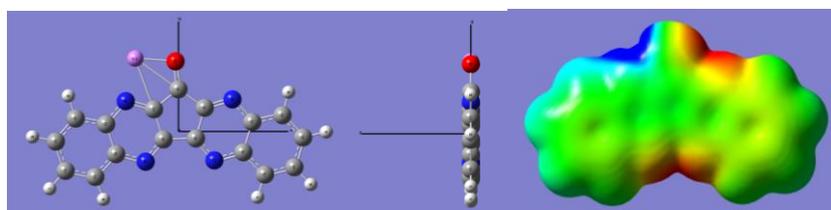| Reaction Level	B3LYP/6-31G(d,p) Cell Voltage at 0K (V)	B3LYP/6-31+G(d,p) in DEE solution Cell Voltage (V) at 298.15K
2Q-Li	3.16	3.06
2Q-Li$_2$	3.14	2.67
2Q-Li$_3$	2.40	2.06
2Q-Li$_4$	0.82	0.90
2Q-Li$_5$	0.65	(not converged)

Figure 5. 2Q-Li structure from G16 optimization and ESP-mapped electronic density.

Figure 8 shows the computational results when a lithium atom reacts with 2Q-Li$_3$ to form 2Q-Li$_4$. Note the molecule mainly retains its planar structure but with a slight curvature and where the new lithium ion resides has turned the ESP surface map blue. Optimizations were also performed where the lithium atom was placed near the center of one of the benzene rings and also near the nitrogen atoms opposite the oxygen atom, but the optimized ground state energies for these configurations were slightly higher than the energy of the one shown in Figure 8.
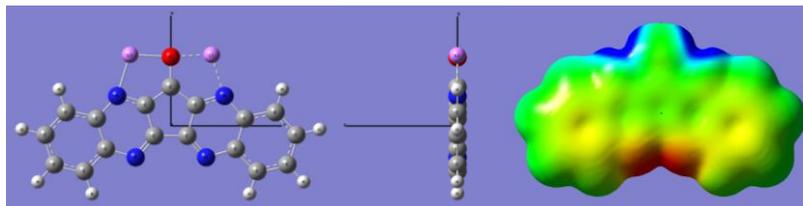
Figure 6. 2Q-Li$_2$ structure from G16 optimization and ESP-mapped electronic density.
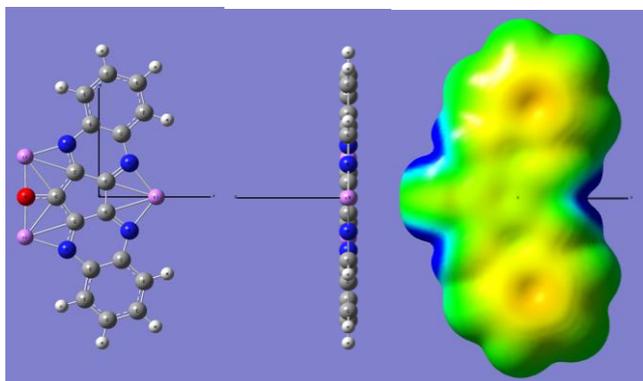

Figure 7. 2Q-Li$_3$ structure from G16 optimization and ESP-mapped electronic density.

Figure 9 shows the computational results when a lithium atom reacts with 2Q-Li4 to form 2Q-Li5. Note the new molecule mainly retains its planar structure but with a slight distortion and where the new lithium ion resides has turned the ESP surface map blue. Optimizations were also performed where the lithium atom was placed near the center of one of the benzene rings and also by placing it near the nitrogen atoms opposite the oxygen atom, but the optimized ground state energies for these configurations were slightly higher than that for the energy of the one shown in Figure 9.Figure 10 shows a plot of the first discharge using 2Q as the active cathode material and the calculated cell (redox) potentials. Note that the calculated cell potentials from Table 2 for 298.15K results in a good indication/trend of the cell potential as a function of state-of-charge.
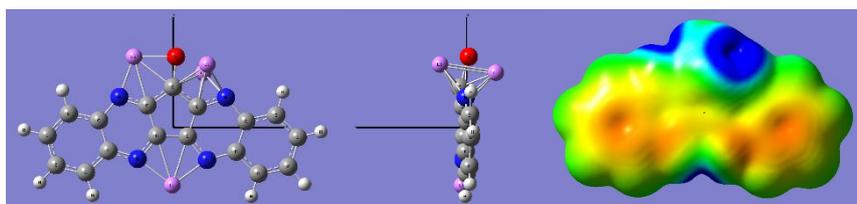

Figure 8. 2Q-Li$_4$ structure from G16 optimization and ESP-mapped electronic density.
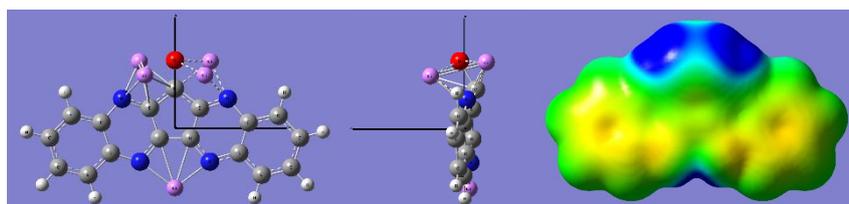

Figure 9. 2Q-Li$_5$ structure from G16 optimization and ESP-mapped electronic density.
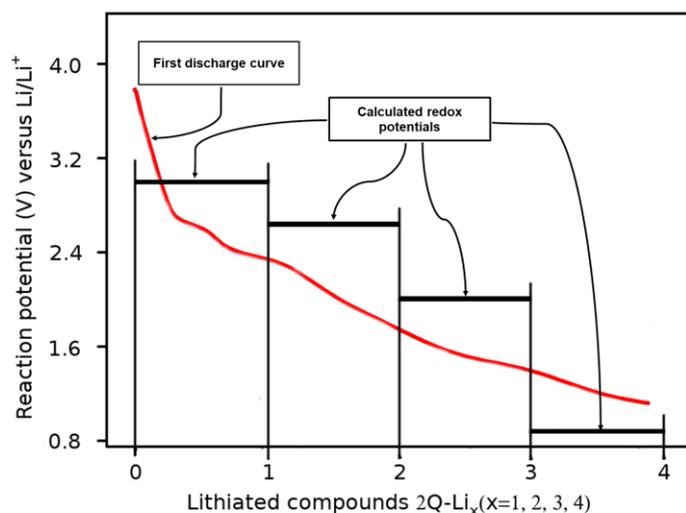
Figure 10. 2Q calculated redox potentials versus experimental results.

III. SUMMARY/CONCLUSIONS

Ab-initio calculations presented herein are in accordance with our theoretical scheme to provide the information about the organic based cathode active materials for the eventual development of future primary and secondary batteries possessing high charge capacity as well as high energy density. Specifically, these Gaussian 16 software based density functional theory calculations show the optimized ground state structures and electrostatic potential electron density surface map contours for $2Q\text{-}Li_x$ (x = 0, 1, 2, 3, 4, 5) representing the nature of molecular structures and the change in the electronic density surface map contours as lithium atoms are caused to intercalate into the 2Q molecular structure. From the free energy computed data at the ground state electronic energy levels at 0K given in Table 1, the calculate e.m.f's or open circuit electric potentials for the Li(s)/2Q(s) cell/battery are shown in Table 2. The cell voltage varies from 3.16 volts for 2Q-Li to 0.65 volts for $2Q\text{-}Li_5$. Similar computed data at 298.15K and shown in Tables 1 and 2 show variation in the open-circuit voltage from 3.06 volts for 2Q-Li to 0.90 volts for $2Q\text{-}Li_4$. Finally, Figure 10 compares the computed data of the open-circuit potentials at 298.15K in the form of a histogram with the experimental data [1] obtained at the cell 1C discharge rate (400 mA g^{-1} active material) as a function of lithium intercalation into $2Q\text{-}Li_x$ (x = 1, 2, 3, 4). The open-circuit computed electric potentials are higher than those experimentally observed (red line) up to x = 3 (as expected). For example at x = 1, ($E_{computed} - E_{experimental}$) $\simeq$ (3.06 − 2.30) = 0.76 volts, the voltage loss associated with the transport of lithium ions, electrons, and the electrochemical polarizations at the interfaces between the cell electrolyte and electrode active materials.

Based on the provided ab-initio analytical data, the deduced general conclusions are given below.

- The preferred site of the first lithium atom for its bonding with the 2Q molecule is in the neighborhood closer to the O atom.
- Bonding of additional lithium atoms involves energetic interactions between the oxygen atom and nitrogen atoms of the π-conjugated hetero-aromatic rings.
- The computed redox potentials of the (Li(s)/2Q(s)) cell are indicative of the observed cell potential as a function of its state-of-charge.
- Organic-based materials for the development of efficient electrodes for primary as well as secondary batteries are recommended compared to inorganic metal oxides because of low cost and the environmentally benign production and disposal of organic compounds.

REFERENCES

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