

Theoretical study of the structure and specific capacity of an organic cathode based on poly(2,5-diaza-1,4-benzoquinone) in a lithiated state

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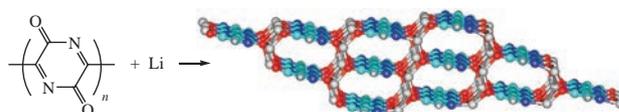
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A density functional theory computational study of poly(2,5-diaza-1,4-benzoquinone) as a potential organic cathode is presented. The lithium insertion in one-dimensional, two-dimensional and three-dimensional models was evaluated and yielded energies of 2.38, 3.12 and 3.59 eV per Li atom, respectively. These values taken together with the specific capacity of ~500 mAh g⁻¹ make poly(2,5-diaza-1,4-benzoquinone) a promising organic cathode material for Li-ion batteries.



The development of organic cathode materials for lithium power sources is of considerable current interest. In comparison with the traditional inorganic cathodes (e.g., LiCoO₂ and LiFePO₄), organic materials have a number of advantages, such as high theoretical specific capacity and environment-friendly production and recycling. Among different types of organic electroactive materials, quinones are probably the most promising due to their high theoretical capacity and reversibility of electrochemical reactions.^{1–3}

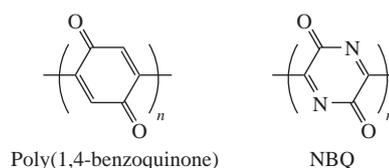
Low-molecular-weight organic compounds are generally highly soluble in dimethyl or ethylene carbonates, so a solid electrolyte has to be applied in order to enable their practical use in lithium power sources. To solve the problem of material solubility, electroactive polymers are used as organic cathodes. In the case of quinones, for both low-molecular-weight^{4,5} and polymer-based^{6–10} materials, the practical capacity decreases noticeably during the cycling, reaching about half the theoretical value within less than 20 cycles. This behavior is partially explained considering that the major fraction of carbonyl groups cannot participate in reversible reactions with lithium.^{11–14}

A rapid fade in the battery capacity during cycling is a common problem of organic cathodes. To address this challenge, it is necessary to reveal the mechanisms of degradation processes and to design new materials with improved properties and stability. In view of a potentially unlimited variety of structures of organic compounds that can become available through chemical synthesis, theoretical calculations can play an important role in the identification of the most promising candidates. Indeed, theoretical calculations allow one to estimate the redox potentials of new molecules^{15,16} and, thus, perform high-throughput screening *in silico*.

Poly(1,4-benzoquinone) has a high theoretical specific capacity of 505 mAh g⁻¹. However, all attempts to apply this compound as a cathode material for batteries were unsuccessful because of low practical capacity and poor operation stability.¹⁸ These problems might be solved using similar materials obtained by

certain modification of the chemical structures of poly(1,4-benzoquinone). It is known, in particular, that the introduction of heteroatoms into the structure of quinones leads to an increase in their reduction potentials^{16,17} due to the chelation of lithium (or sodium) ions, which is reflected in a higher battery voltage.

Here, we report a thorough theoretical study of the new promising cathode material poly(2,5-diaza-1,4-benzoquinone) NBQ, which can be considered as aza-substituted poly(1,4-benzoquinone). In principle, NBQ can be obtained by the oxidative



polymerization of diketopiperazine, a product of the thermal condensation of glycine.

The geometry optimization of the molecules was carried out[†] using the PBE density functional method¹⁹ with SBK pseudopotential²⁰ and an extended basis set C, N, O: [5s, 5p, 2d/3s, 3p, 2d], Li: [4s, 1p/2s, 1p], H: [5s, 1p/3s, 1p] for valence shells implemented in the PRIRODA program package.²¹ Atomic charges were determined by the Hirshfeld charge analysis.²² This approach was successfully used for revealing the degradation mechanism of polyquinone-based cathode material under cycling.²³

The choice of the NBQ structure was motivated by the following considerations. First, the replacement of CH groups with N atoms virtually does not change the molecular weight of the material; thus, the theoretical capacity remains almost as high as for poly(1,4-benzoquinone). Second, the appearance of nitrogen atoms in the *ortho* position to the carbonyl group

[†] All calculations were performed using the facilities of the Joint Supercomputer Center of the Russian Academy of Sciences.

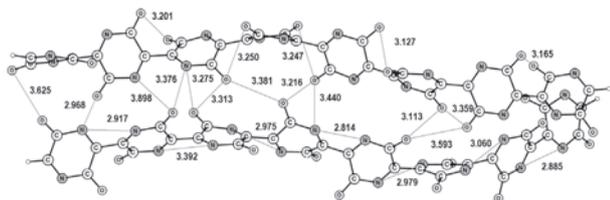


Figure 1 Optimized structure of the dimer $\{(NBQ)_8\}_2$.

increases its affinity for the lithium atom due to the coordination capabilities of the N atom. For instance, the calculated binding energy of the Li_2 molecule to the monomeric 2,5-diaza-1,4-benzoquinone is 5.64 eV, which is 2.44 eV higher than in the case of Li_2 addition to 1,4-benzoquinone. Finally, NBQ represents a conjugated polymer, which is expected to be electrically conductive in a doped state, as supported by the experimental data reported for poly(1,4-benzoquinone)¹⁸ with an analogous π -electron system. Note that the electric conductivity of a cathode is generally provided by the carbon filler, which is usually used in substantial amounts (40–50 wt%). Therefore, the use of a conductive electroactive polymer can additionally boost the capacity in the cathode *via* elimination of functional components accounting for the ballast weight: conductive additives and, perhaps, a polymer binder.

While modeling the polymer chain, oligomers comprising three, four, and eight units were chosen. The preceding theoretical studies of polymerized indolyquinone showed that the redox properties of the material are saturated already for short oligomers with a small number of repeating units.²⁴ Figure 1 shows the structure of the van der Waals dimer $\{(NBQ)_8\}_2$. Because of the repulsion of the O atoms of carbonyl groups, the six-membered rings adopt a nonplanar conformation, which results in the appearance of a local dipole moment. In the helicoidal oligomer with 8 repeating units, the local dipole moments of neighboring rings only partially compensate each other; thus, the total dipole moment amounts to 0.78 Db. An alternative structure with a mutual orientation of the adjacent rings close to the *trans*-configuration (also non-planar) shows similar short contacts between N and O atoms and has a higher energy of 7.1 kcal mol⁻¹. The distances of the intramolecular and intermolecular O–O contacts in the dimer are comparable. There is a notable elongation of the C–C bonds between the neighboring repeating units in the dimer up to 1.506 Å compared to 1.496 Å for the single oligomer chain, which is close to the value of 1.478 Å found in the dimer of benzoquinone.⁵ The observed increase in the C–C bond length seems to be a consequence of the reduction in the electronic coupling between the neighboring repeating units induced by strong intermolecular interactions changing the relative orientation of the rings.

Substantial changes in the NBQ molecular geometry occur because of lithiation. Indeed, the introduction of two lithium atoms

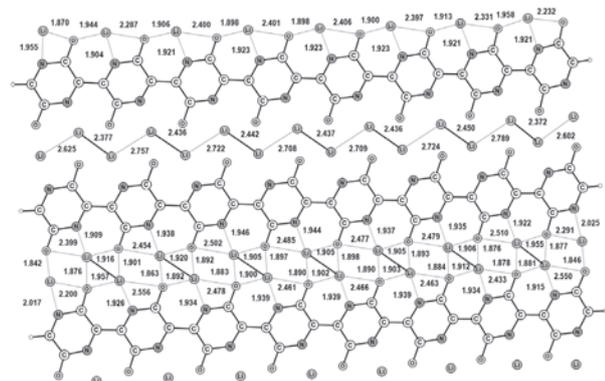


Figure 2 Optimized structure of the lithiated trimer $\{(NBQLi_2)_8\}_3$.

in each repeating unit results in the planar tape-like structure of the polymer (Figure 2) due to the formation of three coordination bonds by each lithium ion: two unequal Li–O (~1.9 and ~2.4 Å) bonds with the O atoms of carbonyl groups from the neighboring polymer chains and an additional Li–N contact (1.92 Å). In case of the lithiated polymer, the bond lengths in the six-membered rings are aligned since their quinoid-type structure was transformed under reduction to an aromatic disubstituted pyrazine. The geometry of the terminal fragments in the lithiated NBQ oligomers is almost the same, and it does not depend on the chain length. This allows one to estimate the specific energy of the NBQ reaction with metallic lithium (ΔE_{Li} per single lithium atom) for an infinite polymer chain:

$$1/2n(NBQ)_n + Li(\text{metal}) = 1/2n(NBQ Li_2)_n + \Delta E_{Li}$$

assuming that a difference between the total lithiation energies of $(NBQ)_4$ and $(NBQ)_3$ is $2\Delta E_{Li}$. While calculating ΔE_{Li} , it is convenient to consider the Li_2 molecule as a source of lithium. Using the experimental data for the lithium sublimation enthalpy²⁵

$$Li(\text{metal}) \rightarrow 0.5Li_2 - 24.9 \pm 0.3 \text{ kcal mol}^{-1}$$

we can obtain the following estimation:

$$\Delta E_{Li} = \Delta E - 0.92 \text{ eV},$$

where ΔE is the calculated specific energy of the lithiation reaction considering Li_2 as a lithium source. Thus, the calculated ΔE_{Li} is 2.38 eV, which corresponds to the potential of 2.38 V for organic cathode against Li^+/Li .

While packing the tape-shaped lithiated oligomer structures in a layer with the formation of intermolecular Li–O coordination bonds (1.89 Å, Figure 2), the geometry of the chains varies slightly with only a small elongation of the C–O bonds by 0.01 Å. Particularly notable is the short distance of ~2.4 Å between the adjacent lithium atoms coordinated with two O atoms of the carbonyl groups belonging to the neighboring NBQ chains. In fact, these short contacts are enforced by the coordination ligand environment, and they do not indicate the formation of real Li–Li bonds. The Mulliken populations of these bonds are even negative (–0.08). The effective charges on the lithium atoms inside the layer and at the edge of the layer are 0.28 and 0.43, respectively. The shortest distances between the O atoms of carbonyl groups within the $\{(NBQLi_2)_8\}_3$ layer are 2.9 Å, which is a bit less compared to the non-lithiated dimer $\{(NBQ)_8\}_2$. The length of the second O...O interlayer contact was 3.4 Å for both lithiated structure and non-lithiated dimer. These results indicate that the introduction of lithium atoms into an organic polydiazabenzquinone cathode occurs with a small volume change.

Within the layer of $\{(NBQLi_2)_8\}_3$, 32 new Li–O coordination bonds are formed with an average energy gain of 0.74 eV (per one bond). These results show that the energy of lithiation substantially increases from 2.38 to 3.02 eV while going from a quasi-one-dimensional structure to the two-dimensional layered system.

At the next stage, one should consider the interaction of the layers of the material in a solid state. We considered the dimer of

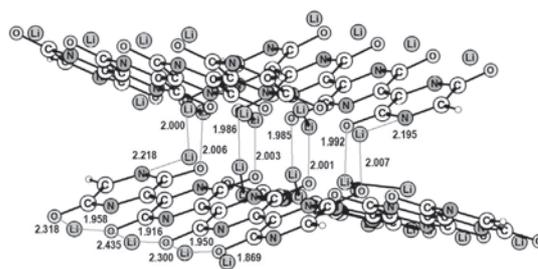


Figure 3 Optimized structure of the model double-layer system $\{(NBQLi_2)_4\}_2 \cdots \{(NBQLi_2)_4\}_2$.

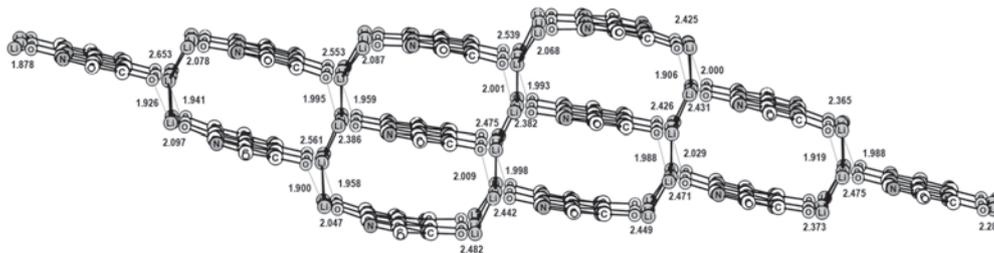


Figure 4 Optimized structure of the model three-layer system $\{(NBQLi_2)_3\}_4 \cdots \{(NBQLi_2)_3\}_4 \cdots \{(NBQLi_2)_3\}_4$.

dimers $\{(NBQLi_2)_4\}_2 \{(NBQLi_2)_4\}_2$ as the simplest model for revealing the interlayer interactions (Figure 3). The interlayer Li–O coordination bonds have an average length of 2.0 Å, which is comparable to the Li–O bond lengths of 1.90–1.96 Å within the layer. The formation of coordination Li–O bonds and repulsion of the rest chemically unbound atoms leads to an inflection of the layers. The calculated interaction energy of the layers gives an average energy gain of 0.35 eV per each new Li–O bond. This value is considerably smaller than that in the case of the two-dimensional structure because of energy losses due to deformation of the layers.

For more complicated three-dimensional models, shorter oligomers of three links were used. Three layer model built from shorter oligomers $\{(NBQLi_2)_3\}_4 \{(NBQLi_2)_3\}_4 \{(NBQLi_2)_3\}_4$ is shown in Figure 4. The coordination polyhedra of the internal lithium atoms differ slightly from that in the simplest three-dimensional model considered above. The interaction energy of the first two layers can be estimated at 10.88 eV. The addition of the next layer leads to a greater energy gain of 11.74 eV since only one layer deforms instead of two in the previous case. The stacking of NBQ layers results in the formation of new Li–O coordination bonds. While estimating the mean energy of the interlayer Li–O bonds in the three-dimensional structure, it is necessary to take into account that each deformation of the layer increases the coordination number of lithium atoms at the adjacent inflection lines up to 5. This gives an additional energy gain of 0.47 eV per one Li atom. Thus, the estimated energy of lithiation strongly increases from 2.38 to 3.59 eV while going from the 1D chain to 2D layer and then to a 3D structure.

In conclusion, the performed quantum-chemical modeling allowed us to identify NBQ, which represents a promising cathode material in terms of both good specific capacity and high energy density. Therefore, it is of interest to consider the Li insertion process under the lithiation of an organic NBQ cathode.

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