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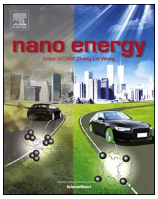

Full paper

Identifying the tuning key of disproportionation redox reaction in terephthalate: A Li-based anode for sustainable organic batteries

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ABSTRACT

The ever-increasing consumption of energy storage devices has pushed the scientific community to realize strategies toward organic electrodes with superior properties. This is owed to advantages such as economic viability and eco-friendliness. In this context, the family of conjugated dicarboxylates has emerged as an interesting candidate for the application as negative electrodes in advanced Li-ion batteries due to the revealed thermal stability, rate capability, high capacity and high cyclability. This work aims to rationalize the effects of small molecular modifications on the electrochemical properties of the terephthalate anode by means of first principles calculations. The crystal structure prediction of the investigated host compounds dilithium terephthalate (Li_2TP) and diethyl terephthalate (Et_2Li_0TP) together with their crystal modification upon battery cycling enable us to calculate the potential profile of these materials. Distinct underlying mechanisms of the redox reactions were obtained where Li_2TP comes with a disproportionation reaction while Et_2Li_0TP displays sequential redox reactions. This effect proved to be strongly correlated to the Li coordination number evolution upon the Li insertion into the host structures. Finally, the calculations of sublimation enthalpy inferred that polymerization techniques could easily be employed in Et_2Li_0TP as compared to Li_2TP. Similar results are observed with methyl, propyl, and vinyl capped groups. That could be a strategy to enhance the properties of this compound placing it into the gallery of the new anode materials for state of art Li-batteries.

1. Introduction

The growing demand for electrochemical storage devices, such as Li-ion batteries, has driven the scientific community to investigate new electrode materials that could provide clean and efficient ways for energy storage [1]. The most common Li-ion based electrodes are mostly involved with the usage of layered oxide compounds such as $LiCoO_2$ or polyanions materials like $LiFePO_4$ [2–4]. Despite good properties in terms of structural stability and energy densities, these compounds suffer from high production cost, due to the scarcity of mineral source, and energetically expensive refining. Finally, difficult and costly recycling and environmental toxicity are also concerns [5]. In this sense, organic matter based electrode materials have emerged as an alternative to the currently used inorganic counterparts [5–7] owing to their natural abundance (cause to inexpensive production), potential of environmental friendliness, easy recycling and mechanical flexibility. Moreover, organic electrode materials require lower temperature for synthesis and refining compare to inorganic electrode materials and they are expected to have a lower carbon dioxide footprint.

The conjugated dicarboxylate family has emerged as an interesting candidate for the use as a negative electrode of advanced Li-ion batteries due to the thermal stability, high charge storage capacity and rate capability and high cyclability [5,8]. For instance, di-lithium terephthalate, $Li_2C_8H_4O_4$, has recently been studied as an alternative to the currently used materials [9]. This compound showed reversible Li intercalation at 0.8 V vs. Li/Li^+ and specific capacities of 300 mAh/g. Moreover, the carboxylate family brings out an advantage concerning the possibility to tune specific properties by molecular design.

Apart from its advantages as promising organic electrode it has inherent drawbacks, which are most common among solid-state organic electrodes, such as low electronic conductivity and dissolution of active molecules into the surrounding electrolyte. To overcome both of the referred issues one solution could be the attachment of the compound to a conducting polymer backbone [10–12]. However, the low solubility of the terephthalate (TP) lithium salts, caused by the strong ionic interaction in its crystal structure, makes processing of the material

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difficult and prevents, for instance, the use of traditional electro-polymerization methods to form the conducting polymer backbone. An approach for enhancing the solubility of these molecules is to modify the molecule by substituting the lithium ion with a small aliphatic carbon chain, thus forming an ester, to diminish the cohesive energy of the crystal structure and hence enhance the solubility of the compound. This laid the foundation of this work by substituting the Li ions on the carboxyl groups by an aliphatic carbon chain. This method must result in highly conjugated compounds with no strong ionic interaction in the crystal that has been shown to be readily polymerizable by traditional methods [10–12].

In this work, we have investigated the effects induced by the addition of aliphatic groups, methyl (Mt), ethyl (Et), propyl (Pr) and conjugated group, vinyl (Vl) in the TP compound. More specifically, we have clarified the mechanisms of ionic insertion in the di-lithium terephthalate ($Li_2C_8H_4O_4$) (denoted as Li_2TP) and its ethylene substituted analogue, diethyl terephthalate ($C_4H_{14}O_4$) (denoted as Et_2Li_0TP). The framework of the density functional theory (DFT) together with an evolutionary algorithm have been applied to resolve the crystal structure changes upon Li insertion in both studied materials and infer the cohesive energy of them. The computation of the redox potential for the Li_2TP predicts a voltage of 0.97 V vs. Li/Li^+ for the first Li insertion and 0.91 V vs. Li/Li^+ for the second Li insertion with a small potential difference of between them, 0.06 V. The ionic insertion mechanism in the ethylene protected TP (Et_2Li_0TP) showed different features when compared to the non-protected compound, Li_2TP. The computed potentials were 1.49 V vs. Li/Li^+ for the first Li insertion and 1.27 V vs. Li/Li^+ for the second Li insertion. The greater separation between the first and second reduction process, 0.22 V, indicates a substantial influence of the small structural modification on the redox reaction. This effect showed to be strongly correlated to the Li coordination number evolution upon the Li absorption into the host structures. We also show by means of quantum chemistry calculations that this effect is not related to the crystallinity. In fact, the addition of the protected group alters the Li-O coordination in such a way that produces the two-step reaction mechanism by stabilizing the intermediate phase.

2. Computational methodology

Density functional theory (DFT) in conjunction with the evolutionary algorithm USPEX [13–15] has been employed in the quest of stable crystal structures of $Li_xC_8H_4O_4$ (x = 2, 3, and 4), $Li_xC_{10}H_{10}O_4$ (x = 0, 1 and 2) and $Li_xC_{12}H_{14}O_4$ (x = 0, 1 and 2). The capability of this method is already proved on the search of complex molecular crystal structures [16,17]. The main idea of this algorithm is to approach the global minimum structure using various selection rules (i.e. variation operator) on a set of randomly created structures. In this study, we have started with an initial population size of 300 structures. The variation operators initially chosen are heredity (fracGene), randomly from the space group (fracRand), softmutation (fracAomsMut), and molecular orientation (fracRotMut). Moreover, we have designed the stopping criteria of the simulation as the appearance of the same structure as the best one for 10 times throughout the generations. Local optimizations of USPEX generated structures were performed on the basis of the density functional theory with the projector-augmented wave (PAW) method as implemented in Vienna ab-initio simulation package (VASP) [18,19]. Spin-polarized generalized gradient approximation was applied in the Perdew, Burke, and Ernzerhof (PBE) [20] parametrization to describe the exchange and correlation term of the Kohm-Sham Hamiltonian. Since pure GGA functional are not suitable to properly explain Van der Walls interactions, we have used the PBE method including the Van der Walls correction within the Grimme's approach (PBE-D2) [21]. The parameters used in the calculation of the energy dispersion in the Grimme's approach are described by following the same strategy as employed in Ref. [17,22] After the evolution process, the selected stable structure was further relaxed until the forces get smaller than 0.01 eV/Å. Moreover, a plane-wave energy cutoff of 600 eV and a k-mesh with the resolution of $2\pi \times 0.08\,Å^{-1}$ was used.

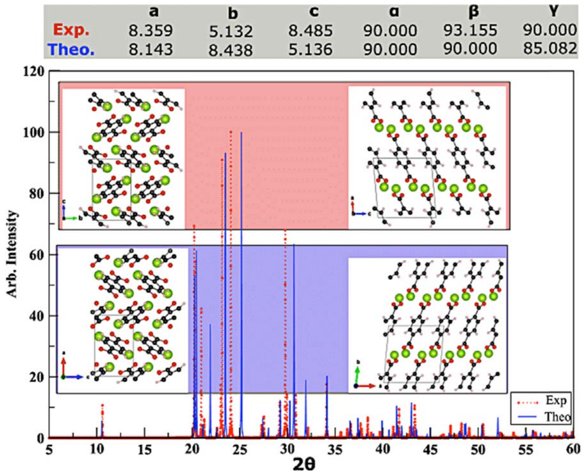

Fig. 1. Comparing XRD pattern between experimental [23] and theoretical structure. Experimental and theoretical structure is shown respectively, in the upper red and lower blue panel.

We have performed ab initio molecular dynamics (AIMD) simulations of 40 ps including the sample equilibration at 300, 600 and 900 K in a canonical ensemble. The high temperatures were chosen to accelerate the dynamical process. After the simulated time scale, no broken bond was observed for the all predicted crystal structures as shown in Fig. S7. This indicates the thermal stability of our predicted structures. Similar strategies has been reported by Seo et. al. to confirm the structural stability of an organic cathode, $Li_4C_6O_6$ [24].

To validate our methodology, the ground state structure of Li_2TP from the evolutionary simulation is compared with the experimentally obtained structure. Fig. 1 shows that the lattice parameters of both structures are comparable with the exchange of crystallographic axis. There is almost negligible difference in the cell volume, only on the order of 0.14%. The XRD pattern is generated by VESTA [25] by considering only the X-ray wavelength of Cu $K\alpha_1$. It can be seen in Fig. 1 that most of the diffraction peaks are well matched. Moreover, in terms of molecular stacking the theoretical structure resembles the experimental γ-stacking. Therefore this well supported theoretical methodology will be employed throughout this study.

The average (de)intercalation potential vs. Li/Li^+ is obtained by computing the Gibbs free energy of the reaction $(y\text{-}x)(Li^+ + e\text{-}) + Li_xC_8H_4O_4 \rightarrow Li_yC_8H_4O_4$; where the difference of y and x is the charge transfer from the Li metal anode to the cathode. The Gibbs free energy is defined as G = E + PV-TS; where E is the internal energy of the system, V is the volume, T is the temperature, P is the pressure and S is entropy. It is observed that for solid systems, the PV and TS contributions of the Gibbs free energy are negligible [26]. Therefore, the internal energy of the system is the main driving component of the Gibbs free energy. Then, the average (de)intercalation potential can be computed without loss of accuracy as:

$$V = -\left\{\frac{E(Li_yC_8H_4O_4) - E(Li_xC_8H_4O_4) - (y-x)E(Li)}{y-x}\right\} \tag{1}$$

where, the total energies, E, were computed by using the framework of the DFT as described above.

Molecular quantum chemistry calculations were performed within the density functional theory framework as implemented in the Jaguar software [27]. The exchange and correlation term of the Kohn-Sham Hamiltonian were described by the B3LYP [28–30] hybrid functional with the 6–311 G** basis set. The implicitly solvent method was employed to have accesses to the solvation energies within the Poisson-Boltzmann self-consistent reaction field method (PBF) [31,32]. The

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