



Exploring the sodium storage mechanism in disodium terephthalate as anode for organic battery using density-functional theory calculations



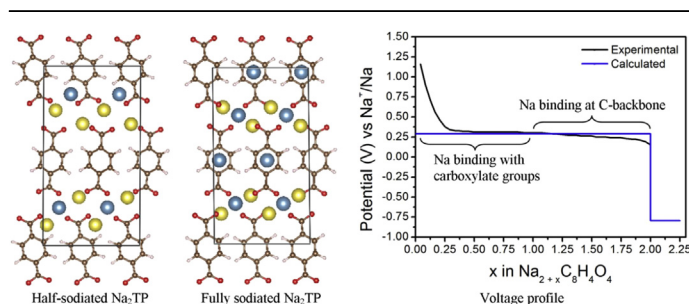
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HIGHLIGHTS

- Na storage mechanism of Na₂TP crystal studied ab initio.
- Na binding at carboxylate sites contributed to initial part of sodiation curve.
- Na binding at hexagonal sites contributed to the second part of the curve.
- Na diffusion barriers can be as low as 0.23 eV in the clean crystal.
- Better prediction of voltage profile with GGA-PBE.

GRAPHICAL ABSTRACT



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ABSTRACT

We present an ab initio study of sodium storage mechanism in disodium terephthalate (Na₂TP) which is a very promising anode material for organic sodium (Na)-ion batteries with reported experimental capacities of ~255 mAh g⁻¹, previously attributed to Na attachment to the two carboxylate groups (coordinating to oxygen atoms). We show here that the inserted Na atoms prefer to bind at carboxylate sites at low Na concentrations and are dominant for insertion of up to one Na atom per molecule; for higher Na concentrations, the hexagonal sites (on the aromatic ring) become dominant. We confirm that the Na₂TP crystal can store a maximum of two Na atoms per molecule, as observed in experiments. Our current results are intriguing as we reveal that the Na binding at carboxylate sites contributes to the initial part of Na₂TP sodiation curve and the Na binding at hexagonal sites contributes to the second part of the curve. The inserted Na atoms donate electrons to empty states in the conduction band. Moreover, we show that the Na diffusion barriers in clean Na₂TP can be as low as 0.23 eV. We also show that there is significant difference in the mechanism of Na interaction between individual molecules and the crystal.

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1. Introduction

Lithium (Li) ion batteries dominate the field of electrochemical energy storage due to their highest energy density and cycle rate

among commercial batteries. The electrodes of commercially available Li ion batteries often include expensive elements and/or toxic components like cobalt. Thus, the inexpensive and environment friendly electrode materials are highly desired for batteries. The focus on the development of new storage materials is shifting from inorganic to organic materials due to high theoretical capacities of organic materials, low-cost, recyclability, possibility of tuning of redox potentials in a wide range by molecular design, and

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abundant resources from renewable natural products or biomass [1–6]. The application of organic materials as battery electrodes is as old as that of inorganic materials. Williams et al. [7] first demonstrated the use of an organic electrode based on a small molecule in 1969. The organic materials which have been considered as electrodes for batteries include organosulfur, organic free radical, organic carbonyl and layered organic compounds, conducting and non-conjugated redox polymers [2,8–13]. Among the organic materials, carboxylate functional groups containing small molecules [4,14] are attractive electrode materials with tunable physical and electrochemical properties. The conjugated dicarboxylate e.g., di-lithium terephthalate ($\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$), di-lithium *trans-trans*-muconate ($\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$) and 2,6-naphthalene dicarboxylate di-lithium (2,6-Naph(COOLi) $_2$) are potential anode materials for Li-ion batteries [4,14]. These conjugated dicarboxylate materials can provide a “green” base for organic batteries as $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ and $\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$ are metabolites of aromatic hydrocarbon oxidation [4] and the terephthalic acid can be produced from recycling of polyethylene terephthalate plastic [4].

Sodium (Na) ion batteries have attracted interest of researchers due to high natural abundance of Na, its low cost and more environment friendliness of Na than Li. Stevens and Dahn [15] in 2000 have demonstrated the use of hard-carbons (pyrolyzed glucose) as high capacity anode materials for rechargeable Na-ion batteries. These materials have reversible capacity of $\sim 300 \text{ mAh g}^{-1}$. However, the majority of electrode materials considered for Na-ion batteries are expensive transition-metal inorganic compounds [16–20]. Zhao et al. [21] and Park et al. [22] demonstrated the use of an organic material disodium terephthalate, Na_2TP , as anode for Na-ion batteries. Na_2TP is a disodium salt of terephthalic acid which is a very promising organic electrode material with reported Na storage capacities of up to two Na atoms per molecule (corresponding to about 255 mAh g^{-1}) [21]. It combines ease of synthesis, environment friendliness, and low cost. The Na storage capacities and voltages of Na_2TP can be manipulated by simple chemical modifications of the terephthalate ion in Na_2TP [22,23]. However, the understanding of Na storage mechanism is currently lacking. It was proposed that the two Na atoms interacted with two carboxylate groups in the Na_2TP molecule during Na insertion process, coordinating to oxygen atoms [21,22]. However, at two inserted Na atoms per molecule, the crystal structure is expected to be severely perturbed. Na binding with the carbon backbone is also possible as shown by theoretical calculations for 2,6-Naph(COOLi) $_2$ intercalated metal-organic framework (iMOF) [14]. The naphthalene C atoms bonded to the carboxylate groups have a negative charge ($\text{C}^{\delta-}$) which contributes to $\text{Li}^+-\text{C}^{\delta-}$ interaction in 2,6-Naph(COOLi) $_2$. In addition, the Li_2TP crystal showed Li storage capacities of ~ 2.3 Li atoms per molecule which hinted that the C-backbone may be important for Li bindings [4]. Thus, it is necessary to understand the Na storage mechanism to design new Na_2TP based materials with higher capacities. Zhang et al. [24] studied Li insertion and diffusion in di-lithium terephthalate (Li_2TP) and di-potassium terephthalate (K_2TP) crystals using density functional theory. However, to the best of our knowledge, there is no reported theoretical study investigating the Na storage mechanism in Na_2TP crystals.

In the present study, we apply density-functional theory (DFT) calculations to understand the Na binding mechanism in the Na_2TP crystal. We observe that the inserted Na atoms interact with carboxylate groups of Na_2TP and convert Na_2TP to Na_{2+1}TP (half-sodiated). Once it is converted to Na_{2+1}TP , Na binding at the hexagonal position of the benzene ring becomes important. We also discuss Na diffusion in clean Na_2TP , Na_{2+1}TP and Na_{2+2}TP (fully sodiated) crystals. Finally, we compare several DFT-based methodologies (DFT with a GGA functional [25], dispersion corrected DFT with the method of Grimme [26], and DFT with two vdW

functional [27]) and suggest the best of these approaches for modelling this type of systems.

2. Computational models and methodologies

The crystal structure of Na_2TP is taken from the work of J. A. Kaduk [28] and optimized with the DFT methods used here (see Fig. 1a). The packing of terephthalate ions in the experimental Na_2TP crystal resembles the β -packing of aromatic hydrocarbons with $a = 3.54804$, $b = 10.81604$, and $c = 18.99430 \text{ \AA}$. The Na atom in the Na_2TP crystal is trigonal prismatic. The two Na–O bond lengths of the Na_2TP molecule in the crystal are 2.43 and 2.72 \AA . The distance between Na atoms and C atoms of the carboxylate groups of Na_2TP molecule in the crystal is 2.89 \AA . The terephthalate ions in the experimental Na_2TP crystal stack like graphite ABA stacking along a -axis. However, the two terephthalate ions along the b axis are not parallel (abbreviated in the following as Na_2TP -non-planar). We have considered another configuration of the Na_2TP crystal, where the two terephthalate ions along the b axis are parallel (abbreviated as Na_2TP -planar) as shown in Fig. 1 b.

The structure optimizations are performed using density functional theory (DFT) [30,31] with the generalized gradient approximation (GGA) and the Perdew-Burke-Eznerhof (PBE) functional (GGA-PBE) [25] as implemented in Vienna ab initio simulation package (VASP) [32–34]. The projector augmented wave method (PAW) [35,36] is used to describe the interaction between the atomic cores and electrons. The valence configurations of the atoms are: carbon (C) $2s^2 2p^2$, hydrogen (H) $1s^1$, oxygen (O) $2s^2 2p^4$ and sodium (Na) $3s^1$. A $6 \times 2 \times 1$ Monkhorst-Pack [37] k -point mesh and a cutoff of 520 eV are used for all the calculations. For bulk Na metal (body-centered cubic, *bcc*) we use a uniform k -point mesh of $11 \times 11 \times 11$. Atomic positions and cell vectors are fully relaxed using the conjugate gradient (CG) algorithm until all force components are less than 0.01 eV \AA^{-1} . The Methfessel-Paxton type broadening of 0.1 eV is used for the partial occupancies. A k -point mesh of $6 \times 2 \times 1$ and a plane wave cutoff of 520 eV provide converged binding energies. The density-of-state (DOS) calculations are performed using Gaussian smearing with 0.1 eV broadening. The Na diffusion barriers are calculated using the climbing-image nudged elastic band (CI-NEB) method [38,39]; the force tolerance considered for the CI-NEB calculations is 0.04 eV \AA^{-1} . The Na binding energies and the voltage curve are calculated using the unit cell of the Na_2TP crystal whereas the Na diffusion barriers are calculated using a larger ($3 \times 1 \times 1$) supercell and a k -point mesh of $2 \times 2 \times 1$.

The average binding energies $E_b^{\text{Na}}(\text{avg.})$ per Na atom are calculated according to eq. (1) [40]:

$$E_b^{\text{Na}}(\text{avg.}) = (E_{\text{Na}_2\text{TP}+n\text{Na}} - E_{\text{Na}_2\text{TP}} - nE_{\text{Na}})/n, \quad (1)$$

where $E_{\text{Na}_2\text{TP}+n\text{Na}}$ is the total energy of the Na_2TP crystal with ‘ n ’ the number of inserted Na atoms, $E_{\text{Na}_2\text{TP}}$ is the total energy of the clean Na_2TP crystal, and E_{Na} is the total energy of a single Na atom in vacuum. The negative values of $E_b^{\text{Na}}(\text{avg.})$ indicate thermodynamic preference for Na atom insertion. We have considered non-spin polarization calculations as we confirmed that the inclusion of spin-polarization has negligible effect on the calculated binding energies.

To investigate the phase segregation of Na_2TP during Na insertion process, we have calculated the formation energy of Na_{2+x}TP per formula unit according to eq. (2) with respect to the clean Na_2TP crystal and bulk Na *bcc*.

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