A theoretical method to predict novel organic electrode materials for Na-ion batteries

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ABSTRACT

Currently known organic electrode materials for lithium-ion batteries have severe cost and resource constraints and are difficult to implement in applications for large-scale electrical energy storage. Compared to lithium-ion battery electrode materials, sodium-ion battery electrode materials are more abundant and more cost effective. However, methods for the prediction of organic electrode materials for sodium-ion batteries are not perfect at present. A fast and accurate theoretical method for finding possible candidates for organic electrode materials for Na-ion batteries is urgently needed. In the present work, dispersion-corrected hybrid density functional theory is applied to study five organic electrode materials for Na-ion batteries. The results of this study show that the D2 dispersion-corrected hybrid functional method (HSE06-D2) can precisely calculate the potential of organic materials with a small average error of approximately 3.68%. The band gap values are approximately lower than 2.5 eV, which proves that the materials have good conductivity and are expected to be candidates for organic electrode materials for sodium-ion batteries.

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1. Introduction

The sodium-ion battery [1,2] was originally researched in the late 1970s and 1980s in conjunction with the lithium-ion battery [3,4]. The advantages of lithium-ion batteries, namely, its higher energy density as a result of its higher potential and lower molecular mass, shifted the focus of battery research to lithium-ion batteries. Although current lithium-ion battery technology is quite mature, there are still many problems with lithium-ion batteries, such as poor security, short life, low temperature performance and high cost. In addition, due to the low relative abundance and uneven distribution of lithium in nature, the rising demand for lithium resources has led to price increases. Therefore, it is urgent to explore rechargeable battery electrode materials based on abundant resources that have low cost, high safety performance and stable cycling performance [5].

Due to the abundance of sodium and the similar electrochemical properties of lithium and sodium insertion in organic compounds, sodium-ion batteries have the potential to meet large-scale grid energy storage needs [6–8]. There is much work to be done in the field of Na-ion batteries in order to catch up with Li-ion battery technology, of which new prediction methods for

electrode materials will be the key to successful Na-ion batteries. In the past couple of years, the sodium-ion battery field [9] has demonstrated many compatible electrode materials [10–12]. In this paper, we mainly study sodium-ion battery organic electrode materials that contain carbon-oxygen double bonds (C=O), where the reaction process of these materials can be simply summarized by the Na ion penetration process, in which the double bond (C=O) is reduced to a single bond (C—O), and the Na ion embedding process, in which the single bond (C—O) is oxidated to a double bond (C=O).

Thus far, millions of organic materials have been reported, and many of them can store Na ions. At present, a fast and accurate method to find possible candidates for electrode materials is urgently needed. Recently, several density functional theory (DFT) methods containing van der Waals (vdW) force corrections have been developed and can be used to calculate the vdW force between molecules in organic electrode materials. These methods have been applied to the calculation of lithium-ion batteries, for example, the PBE-D2 method was used to predict the reaction potential and intermediate state structure in the charge/discharge process of $C_{18}H_{12}Li_2O_8 \cdot 4H_2O$ [13]. PBE-D2 was also applied to calculate the lithium ion diffusion mechanism in $C_{12}H_4N_4$ [14], and 31 kinds of novel organic electrode materials were predicted [15].

In addition to the D2 dispersion-corrected method, there are several other methods for calculating vdW interactions, including

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Table 1
Some properties of the five materials are listed, and theoretical capacity is calculated according to C = nF/M (where F is the Faraday constant, M is the relative molecular mass, and n is the electron transfer number per formula).

| Material	Theoretical Capacity ($Ah \cdot kg^{-1}$)	Average experimental Potential (V)	Space group	Optimized Lattice parameters	
				Before Sodium Insertion	After Sodium Insertion
ANTQUO	214.00	1.90 [17]	P21/a	a = 15.33 Å, b = 3.62 Å, c = 7.61 Å α = 90.00°, β = 102.88°, γ = 90.00° 411.61 Å^3 (Volume)	a = 14.84 Å, b = 3.93 Å, c = 7.82 Å α = 90.00°, β = 106.08°, γ = 90.00° 438.64 Å^3 (Volume)
SINDIG	181.12	1.96 [16,19]	P21/c	a = 7.52 Å, b = 3.71 Å, c = 19.58 Å α = 90.00°, β = 93.82°, γ = 90.00° 544.73 Å^3 (Volume)	a = 7.94 Å, b = 3.77 Å, c = 19.04 Å α = 90.00°, β = 96.39°, γ = 90.00° 560.23 Å^3 (Volume)
INDIGO	110.00	1.80 [18]	P21/c	a = 17.70 Å, b = 7.54 Å, c = 6.01 Å α = 90.00°, β = 96.70°, γ = 90.00° 777.36 Å^3 (Volume)	a = 17.58 Å, b = 7.95 Å, c = 5.81 Å α = 90.00°, β = 97.57°, γ = 90.00° 797.17 Å^3 (Volume)
LENPEZ	140.00	2.20 [21]	P21/n	a = 4.57 Å, b = 14.29 Å, c = 10.24 Å α = 90.00°, β = 85.85°, γ = 90.00° 662.40 Å^3 (Volume)	a = 4.60 Å, b = 14.53 Å, c = 10.22 Å α = 90.00°, β = 87.04°, γ = 90.00° 681.33 Å^3 (Volume)
TCBENQ	161.00	2.72 [20]	P21/a	a = 8.51 Å, b = 5.56 Å, c = 8.37 Å α = 90.00°, β = 105.84°, γ = 90.00° 381.09 Å^3 (Volume)	a = 10.18 Å, b = 5.71 Å, c = 7.71 Å α = 90.00°, β = 104.44°, γ = 90.00° 434.58 Å^3 (Volume)
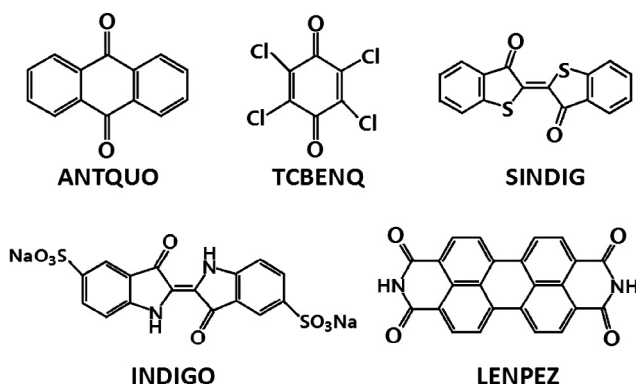
Fig. 1. The molecular structures of the five organic materials.

the D3 method, which is a higher order dispersion correction compared to D2 and other vdW-DF methods. The D3 method can be used to predict the potential of organic electrode materials better than the PBE-D2 method, and its use in the prediction of materials for lithium-ion batteries has been confirmed [16]. However, calculations of organic electrode materials for sodium-ion batteries have not been improved. Therefore, this present work examines in detail theoretical methods for the study of organic electrode materials for sodium-ion batteries.

In this paper, five organic crystalline materials containing carbonyl groups were selected from the organic molecular crystal structure database (CCDC, Cambridge Crystallographic Data Centre), and a series of related calculations were carried out. The five materials are anthraquinone (ANTQUO [17], $C_{14}H_8O_2$), indigo carmine (INDIGO [18], $C_{16}H_8N_2Na_2O_8S_2$), thioindigo (SINDIG [16,19], $C_{16}H_8S_2O_2$), tetrachloro-p-benzoquinone (TCBENQ [20], $C_6Cl_4O_2$), perylene-3,4,9,10-tetracarboxylic acid diimide (LENPEZ [21], $C_{24}H_{10}N_2O_4$).

2. Calculation method

The theoretical calculations are performed using the Vienna Ab initio Simulation Package (VASP [22]). The projected-augmented wave (PAW [23]) method is applied to treat ion-electron interactions. The plane-wave cutoff energy is assigned to be 400 eV. In addition, at least 0.0001 eV per atom is used as the standard for

self-consistent convergence of the total energy. For the geometric optimization, the k-point grid in reciprocal space is set as shown in Table 1.

The exchange-correlation energy of electrons is treated using the generalized gradient approximation (GGA [24]). In addition to the GGA, hybrid functionals can improve the long-range exchange calculation between two electrons due to the exact exchange potential. Therefore, the calculation method used in this paper considers two kinds of hybrid functional potentials, i.e., PBE0 [25–27] and HSE [28,29]. For the vdW correction, non-local DFT using a correlation functional (vdW-DF [30]) and dispersion-corrected DFT-D [31–35] (DFT-D2 and DFT-D3) are adopted.

3. Results and discussion

Using the method of average voltage calculated by Sun et al. [36], the reaction voltage is given by the Gibbs free energies before and after reaction, and the voltage can be expressed by:

$$V = -\frac{E_{Na-M} - E_M - nE_{Na}}{nF}$$

where n is the number of charges transferred during the reaction, F is the Faraday constant, E_{Na} and E_M are the free energy of the sodium crystal and the organic molecular crystal before the reaction, respectively, and E_{Na-M} is the total energy after the reaction.

Fig. 1 illustrates the molecular structures of the five organic materials, and Table 1 lists some of their relative physical properties. After sodium insertion, for the five organic crystals, the unit cell volumes are generally increased smaller than 5%, while the crystal lengths in some directions are contracted obviously, which may be attributed to the strong ionic interaction between Na ion and O ion in the direction.

The experimental and theoretical potential values of each of the five materials obtained by different calculation methods and the average error between the theoretical and experimental values are exhibited in Figs. 2 and 3, respectively. The average calculation error of the PBE functional is the largest at approximately 34.8%. Based on past experience, the binding energy between molecules calculated using the PBE functional is too low to accurately predict the potential of organic electrode materials. For the other two hybrid functional methods, PBE0 and HSE06, the average errors are 27.2% and 26.0%, respectively, which are smaller and therefore better than those of PBE. The calculation results of these two methods, in which only the exchange energy is considered without tak-