Hybrid Functional Study on Small Polaron Formation and Ion Diffusion in the Cathode Material Na₂Mn₃(SO₄)₄

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ABSTRACT: The crystal structure, electronic structure, and diffusion mechanism of Na ions in the cathode material Na₂Mn₃(SO₄)₄ are investigated based on the Heyd–Scuseria–Ernzerhof hybrid density functional method. The simultaneous motion model of polaron–sodium vacancy complexes was used to reveal the diffusion mechanism of Na ions in this material. Polaron formation at the Mn third-nearest neighbor to the Na vacancy was found. Two crossing and two parallel elementary diffusion processes of the polaron–Na vacancy complex were explored. The most preferable elementary diffusion process has an activation energy of 852 meV, which generates a zigzag-like pathway of Na-ion diffusion along the [001] direction in the whole material. Possessing a voltage of 4.4 V and an activation energy of 852 meV, Na₂Mn₃(SO₄)₄ is expected to be a good cathode material for rechargeable sodium ions.

INTRODUCTION

During the past decade, searching cathode materials for sodium-ion batteries (SIBs) has become a new attractive direction. The key reasons to explain this trend are based on sodium’s properties and its natural availability. Many recent studies figured out that although Na ions possess larger radii and heavier ion weight than Li ions (r_Na = 0.98 Å, m_Na = 23 g/mol, and r_Li = 0.69 Å, m_Li = 6.9 g/mol), Na ions can diffuse effortlessly inside electrodes, and sodium-based materials own significantly different voltages compared with analogous lithium compounds. Several groups of sodium-based materials have been classified by their compositions and structures, such as oxide NaₓMO₂ (where M is V, Mn, Fe, Co, and Ni), hydroxide NaₓFe(P₂O₇)ₓ⁻, phosphate (olivine/maricite NaMPO₄ₓ, NASICON Na₃M₂(PO₄)₆, and NaVOPO₄), pyrophosphate NaₓFeP₂O₇, sulfate Na₃Mn(SO₄)₄, carbonate Na₃MnPO₄CO₃, and organic materials. The entire voltage in the range of 2.0–4.5 V of the abovementioned materials is just 0.18–0.57 V lower than that of lithium materials with similar structures. Moreover, the amount of sodium precursor is almost infinite, whereas the lithium resource in the earth is limited, leading to the fact that its raw material price is about 10–60 times lower than that of lithium. For example, the price of lithium carbonate is about 4.11–4.19 €/kg, whereas it is 0.07–0.37 €/kg for sodium carbonate. As a consequence, the prices of SIBs are estimated to be much lower than those of lithium-ion batteries. SIBs are expected to become the next generation of ion-rechargeable batteries.

Among the materials applied for SIBs, sulfate-based polyanion compounds have drawn much attention because of the high redox potential. Many distinct structures containing sulfate groups have been reported, such as eldellite NaFe(SO₄)₂, alluaudite Na₂Mn(SO₄)₃, and krohnkite Na₂M(SO₄)₂·2H₂O (where M is a transition metal). Experimentally, the orthorhombic structure of Na₂Mn₃(SO₄)₄ was synthesized first time in 2016 and evaluated as a promising cathode material with voltage up to 4.4 V. The structure of this material contains the tunnels which encourage Na ions to diffuse easily inside. Although the bond valence map (BVM) method was employed to predict the most preferable diffusion direction, the diffusion mechanism has yet to be explained clearly. Thus, an intensive investigation is necessary to fully evaluate the electrochemical performance of this compound.

During the diffusion of Li/Na inside the inorganic cathode materials, a small polaron is treated as an important factor which intensely affects the charging and discharging processes. Up until 2006, Ceder et al. employed the density functional theory (DFT) to provide the evidence of the small polaron formed by self-trapped charges caused by the lattice distortion in the defect structure of LiMnPO₄ and came to conclusion of a strong polaron–Li ion interaction because of a binding energy of approximately 500 meV. Based on the finding of the prior research, Ellis et al. and Mauger et al. individually explained their experimental results of slow charge carrier migration in LiMnPO₄ (E_a = 775 meV) and LiFePO₄ (E_a = 665 meV), respectively, by taking into account the magnetic polaron effect. Later in 2011, Ong et al. reported an activation energy of 303 meV (196 meV) and 170 meV (133 meV) for...
the free positive (negative) polaron migration in LiFePO₄ and LiMnPO₄ respectively.25 Obviously, the polaron migration makes an undeniable contribution to the overall diffusion mechanism of the charge carriers inside cathode materials. Afterward, Dinh et al. proposed a complex diffusion model in which the Li-/Na-ion diffusion is treated as an elementary diffusion process (EDP) and in which Li/Na diffusion is accompanied with a simultaneous migration of the small polaron.26,27 Three EDPs, including the single, crossing, and parallel processes, are assumed in revealing that the diffusion pathways and the diffusion processes in the whole material are treated as combinations of EDPs. The hypothesis of the Li/Na ion—small polaron complex diffusion after this was applied to several types of cathode materials to explore the diffusion mechanism and acquire reasonable results.7−9,11,26−29

The comprehensive investigation to clarify the diffusion mechanism of the Na ion—polaron complex in inorganic materials would be indispensable to simulate accurately their electrochemical properties. Herein, we employ this hypothesis to investigate the diffusion mechanism of Na ions in Na₂Mn₃(SO₄)₄.

■ RESULTS AND DISCUSSION

Crystal and Electronic Structures. The Na₂Mn₃(SO₄)₄ system in the Cmc2₁ orthorhombic group31 has a unit cell containing 12 distorted MnO₆ groups, the corners of which share with the other MnO₆ octahedron and SO₄ tetrahedron, as illustrated in Figure 1. In order to determine the most stable magnetic arrangement of Mn ions, the total energy of the different magnetic configurations—antiferromagnetic (AFM), ferromagnetic (FM), and nonmagnetic (NM)—was calculated. As the Heyd–Scuseria–Ernzerhof hybrid density functional method (HSE06) and the general gradient approximation (GGA) method with an addition of Hubbard-like term U (GGA + U method) give the same trend in determining the stable alignment of Mn ions for the pristine structure Na₂Mn₃(SO₄)₄, in order to save the computation cost, we employed the GGA + U method (U = 3.9 eV) to explore the most stable structure. For the AFM alignment, we considered four configurations of Mn magnetic moments, namely AFM₁, AFM₂, AFM₃, and AFM₄, as illustrated in Figure S1. Among the four AFM configurations, AFM₃ has the lowest total energy which is lower than that of AFM₁, AFM₂, and AFM₄ by an amount of 25.0, 25.1, and 21.5 meV, respectively. The total energy of FM alignment is insignificantly higher than that of AFM₃ by 40 meV and considerably lower than that of NM configuration by 58.15 eV, which implies that both the FM and AFM configurations can be considered as stable spin alignments, and the calculated results of polaron formation and ion diffusion for these two cases are similar,29 therefore, we chose the FM configuration for convenience. The stable structure in the FM alignment was fully optimized by the HSE06 method and used hereafter in our calculation.

The lattice parameters are listed in Table 1. The data show a good agreement between calculations and experiments. The calculated lattice parameters by HSE06 show a good agreement with experiments. Along the [001] direction, each MnO₆ group shares two axial O corners with two other MnO₆ groups to form zigzag chains. Each MnO₆ octahedron also shares an edge with one SO₄ tetrahedron. Moreover, each chain connects to the others through the small chains (−SO₄−MnO₆−)₂ and (−SO₄−MnO₆−MnO₆−SO₄−), which arrange along the [100] direction. The MnO₆−MnO₆ dimer links with each other via sharing an O ion with the SO₄ group. The complex three-dimensional framework created by the MnO₆ and SO₄ groups forms tunnels along the [001] direction in which Na ions are inserted.

In the framework of Na₂Mn₃(SO₄)₄, two types of distorted MnO₆ octahedron with different Mn−O bond lengths and O−Mn−O bond angles are distinguished. Table 2 shows the bond lengths of Mn−O in these octahedrons. The bond lengths in the first type of Mn(1)O₆ are in the range of (2.067−2.345) Å, whereas the bond lengths of the second one are from 2.066 to 2.496 Å, the longest bond of which is significantly longer than that of the first one. As a result, the average bond length of the former type is 2.163 Å, which is 0.016 Å shorter than that of the latter. Using the formula of the degree of distortion, \( \Delta = 1/\delta \sum_{n=1}^{\delta} \left[ (d_n - \langle d \rangle)/\langle d \rangle \right]^2 \), where \( d_n \) and \( d \) are the MnO bond length and the average one, respectively.\(^{11}\) The degree of distortion (\( \Delta \)) of the Mn(1)O₆ octahedron (\( \sim 2 \times 10^{-3} \)) is smaller than that of Mn(2)O₆ (\( \sim 4 \times 10^{-3} \)). The first Mn(1)O₆ type creates a dimer [Mn(1)O₁₂] and an alternative (−SO₄−Mn(1)O₆−) along the [100] direction. On the other hand, the second Mn(2)O₆ groups are connected by sharing two O atoms at two opposite axial sites to set up an infinite zigzag chain [Mn(2)O₁₀₆] along the [001] direction.

Figure 2 illustrates the density of states (DOSs) of FM Na₂Mn₃(SO₄)₄ calculated by the HSE06 method. As shown in Figure 2a, the states of oxygen 2p electrons dominantly distribute to the valence band (VB), whereas the 3p electrons of S occupy states in an energy region lower than −7.0 eV. The 3d orbitals of Mn occupy mainly the conduction band and the state just below the Fermi level. Therefore, the 3d orbitals of Mn ions would primarily determine the electronic properties of this material. The calculated band gaps of the up-spin and down-spin channels of Na₂Mn₃(SO₄)₄ are 5.9 and 7.8 eV.

| Table 1. Lattice Parameters and Volume of Ferromagnetic Na₂Mn₃(SO₄)₄ |
|-------------------|---------|---------|---------|---------|---------|---------|---------|
|                   | \( a \) | \( \Delta \) | \( b \) | \( \Delta \) | \( c \) | \( \Delta \) | \( V \) | \( \Delta \) |
| Exp.\(^{21}\)     | 14.831  | 0.00    | 9.911   | 0.00    | 8.685   | 0.00    | 1276.47  | 0.00    |
| FM                | 14.543  | −1.93   | 9.744   | −1.68   | 8.566   | −1.36   | 1213.85  | −4.91   |

\(^{28}\)Derivation \( \Delta \) of the calculated values in comparison with experiment is in percentage (%).
The two-step redox potentials called small polaron,\textsuperscript{23} which forms because of the defect discharging processes, may strongly affect the diusion because of the absorption of electro-

V = \( E[Na_{2-y}Mn_y(SO_4)_4] + (x - y)E[Na] \) 

where \( E[Na_{2-y}Mn_y(SO_4)_4] \) and \( E[Na] \) are the total energies of \( Na_{2-y}Mn_y(SO_4)_4 \) and \( Na \) metal, respectively, and \( \epsilon \) is the absolute electron charge. The two-step redox potentials corresponding to the processes Mn\textsuperscript{2+} to Mn\textsuperscript{3+} (for \( x = 2, y = 1 \)) and Mn\textsuperscript{3+} to Mn\textsuperscript{4+} (\( x = 1, y = 0 \)) are 4.3 and 4.5 V, respectively. The redox potential of the process Mn\textsuperscript{2+} to Mn\textsuperscript{3+} (\( x = 2, y = 0 \)) is 4.4 V, which is consistent with the previous work.\textsuperscript{21} These results suggest that the average open-circuit voltage of \( Na_{2}Mn(SO_4)_4 \) can gain 4.4 V.

**Formation of Small Polaron.** A quasi-particle, the so-called small polaron,\textsuperscript{23} which forms because of the defect caused by the removal or insertion of Na ions during charging/discharging processes, may strongly affect the diusion mechanism of Na ions. In the cathode materials, when an electron or a hole is introduced into the material, a small polaron would form. In \( Na_{2-y}Mn_y(SO_4)_4 \), when a Na atom is removed, a hole is introduced in the system, leading to the fact that the nearest Mn\textsuperscript{2+} ion is oxidized to Mn\textsuperscript{3+}, which causes a local distortion in the MnO\textsubscript{6} octahedron because of the shrinking of the Mn–O bond lengths. Hence, a charge carrier (hole) would be self-trapped at the Mn\textsuperscript{3+} site, that is, a small polaron forms at this position, as stated in previous works.\textsuperscript{5,9,26–29}

In order to find the polaron site, we calculate the Mn–O bond lengths and the magnetic moment of the nearest Mn ions to the vacancy. There are three nearest-neighbor Mn ions (denoted as 1NN, 2NN, and 3NN) around a Na ion at distances of 3.473, 3.486, and 3.642 Å, respectively. When a Na ion is deintercalated, there is a significant change at the 3NN Mn site, that is, the average bond length Mn–O is shrunk from 2.16 to 2.03 Å and the Mn magnetic moment decreases from 3.77 to 2.94 \( \mu_B \). It implies that a local distortion appears around the 3NN site and a hole is self-trapped at this site. It should be noted here that, in order to find exactly the site where the polaron favorably forms, one should compare the total energies of three configurations corresponding to the formation of polaron at 1NN, 2NN, and 3NN to the Na vacancy, respectively. Our calculation for the three cases of polaron formation at 1NN, 2NN, and 3NN to the Na vacancy shows that the total energy of the polaron formed at the 3NN site is considerably lower than those at 1NN and 2NN by an amount of 219 and 74 meV, respectively. In addition, it should be emphasized that, similar to olivine phosphate LiMnPO\textsubscript{4},\textsuperscript{26} because of the overestimation of orbital delocalization, GGA + \( U \) fails in describing the bound states of 3d Mn ions in the vacancy structure. Figure S2 shows the clean band gap without any bound state, which is caused by the local distortion and the oxidation of Mn ion from Mn\textsuperscript{2+} to Mn\textsuperscript{3+} when a Na ion is removed. It suggests that GGA + \( U \) (and GGA) may underestimate the activation energy of Na diffusion because it ignores the polaron contribution in diusion processes.

The change in crystal structure results in a substantial adjustment in the electronic structure. Figure 2b shows the DOS of the defect structure with the removal of a Na ion. As can be seen in Figure 2b, five sharp peaks of DOS appear in the band gap. Four sharp peaks of down-spins are caused by the Jahn–Teller deformation effect of the Mn\textsuperscript{3+}O\textsubscript{6} octahedron. One peak of up-spin at a lower energy level in the band gap is the d state shifting from the VB because of a hole introduction. The appearance of this spin-up peak is caused by the shifting of one electron of 3NN Mn to the Na vacancy from its state below the Fermi level to occupy a bound state inside the band gap, resulting in the change of oxidation of 3NN Mn\textsuperscript{2+} ion to 3+. Hence, the peak at the lowest energy (1.6 eV) indicates the occurrence of a bound state reflecting the formation of a polaron accompanying to the Na vacancy. To conclude, the changes in the crystal and electronic structure provide convincing evidence that one small polaron forms at the Mn third-nearest neighbor to the Na vacancy when a Na vacancy appears in \( Na_{2}Mn(SO_4)_4 \).
Finally, we investigate the diffusion mechanism of Na ion in the full discharge state. For this aim, we first determine all of the possible EDPs inside this material. Diffusion of Na ion is considered as a complex process of Na vacancy and its accompanying polaron. The hypothesis of EDPs of Na vacancy–small polaron complexes$^{26}$ is applied to explore the Na-ion diffusion inside the material. According to Dinh et al.$^{26}$ there are three kinds of EDP occurring in the cathode materials; the parallel (crossing) process occurs when the polaron hopping path from a Mn site to the adjacent Mn site is parallel (crossly) to the Na vacancy diffusion direction. On the other hand, the single process takes place when the polaron does not hop during the Na vacancy movement. Based on the arrangement of the Na ion and polyanion framework in the symmetrical crystal structure of Na$_2$Mn$_3$(SO$_4$)$_4$, it is obvious that the single process could not occur.

Figures 3 and 4 demonstrate the pathway and activation energy profile of the EDPs, respectively. Four feasible EDPs between two adjacent Na vacancies were considered.

Process p1: As illustrated by Figure 3a, Na vacancy migrates from the Na1 site to Na6 site, whereas the polaron hops from the Mn8 to Mn3 site in parallel with the direction of Na diffusion. This process is a parallel process with the reaction coordinate of 7.2 Å and activation energy of 864 meV, as demonstrated by the curve 16-p1 of Figure 4.

Process p2: In the process illustrated in Figure 3b, the Na vacancy diffuses from the Na1 site to Na4 site with a distance of 7.1 Å, whereas the accompanying polaron hops from the Mn5 site to the Mn8 site in parallel with the moving direction of Na. This process is a parallel process with an activation energy of 1.190 eV (curve 14-p2 of Figure 4).

Process c1: Figure 3c demonstrates the process in which the polaron jumps from the Mn8 site to the Mn1 site during the movement of Na vacancy from the Na1 site to the Na8 site. The reaction coordinate of the diffusing path of Na ion is 9.5 Å. Because the hopping path of the polaron crosses the moving way of Na vacancy, this process is treated as a crossing process.

Process c2: Figure 3d illustrates the other crossing process which takes place when a Na vacancy diffuses from the Na6 site to the Na8 site and the polaron jumps from the Mn3 to Mn1 site. Within the distance of 8.3 Å, the activation energy is 852 meV (curve 68-c2 of Figure 4).

Overall, the activation energy required for this EDP is 1.078 eV (curve 18-c1 of Figure 4).

Process c2: Figure 3d illustrates the other crossing process which takes place when a Na vacancy diffuses from the Na6 site to the Na8 site and the polaron jumps from the Mn3 to Mn1 site. Within the distance of 8.3 Å, the activation energy is 852 meV (curve 68-c2 of Figure 4).

The diffusion pathways of Na ions in the whole material can be explored by combining the preferable EDPs. Clearly, the process c2 needs the lowest activation energy of 852 meV for Na vacancy diffusion; hence, c2 would be the most preferable EDP. The repetition of process c2 creates a zigzag-like diffusion path along the [001] direction, as illustrated in Figure 5, forming the most favorable diffusion pathway of Na ions in this compound. Diffusion of Na ion along this pathway has an activation energy of 852 meV, which is consistent with the experimental value (620 meV at 300 K) measured by the impedance spectroscopy measurement and the BVM meth-
Na2Mn3(SO4)4 is expected as a promising candidate for the Mn third-nearest neighbor to the Na vacancy. As the Na ion unassistedly migrate via the four elementary diffusion processes: two parallel and two crossing processes. Among these processes, the crossing process c2 is the favorable one because of its lowest activation energy. Na ions in this material favorably diffuse along a zigzag-like path along the [001] direction, with an activation energy of 852 meV. Possessing a high operating voltage and a diffusion pathway with an activation energy relatively compared with olivine phosphate LiFePO4 which possesses an activation energy of 630 meV, Na2Mn3(SO4)4 would possess quite similar electrochemical properties.

■ CONCLUSIONS

We have systematically investigated the crystal structure, electronic structure, the formation of polaron, and explored the diffusion mechanism of Na ions in Na2Mn3(SO4)4 by employing an accurate calculation method (hybrid functional method HSE06). At the ground state, Na2Mn3(SO4)4 was predicted to be stable in FM and AFM states. The achievable voltage of the material is 4.4 V. As a Na ion is removed from the system, a small polaron would form and contribute to the diffusion process of the Na ion. A polaron was found to form at the Mn third-nearest neighbor to the Na vacancy. As the Na vacancy diffuses, the accompanying polaron would simultaneously migrate via the four elementary diffusion processes: two parallel and two crossing processes. Among these processes, the crossing process c2 is the favorable one because of its lowest activation energy. Na ions in this material favorably diffuse along a zigzag-like path along the [001] direction, with an activation energy of 852 meV. Possessing a high operating voltage and a diffusion pathway with an activation energy relatively compared with olivine phosphate, Na2Mn3(SO4)4 is expected as a promising candidate for cathode materials of rechargeable sodium-ion batteries.

■ COMPUTATIONAL METHOD

Present calculations are based on the Heyd–Scuseria–Ernzerhof hybrid functional HSE06 method implemented in the Vienna Ab initio package.22–34 The hybrid functional HSE06 method approximates the exchange correlation energy \( E_{xc} \) by incorporating a certain amount of the exact exchange Hartree–Fock (HF) energy \( E_{xc}^{HF} \) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation energy determined by DFT in the following form

\[
E_{xc}^{HSE} = aE_{xc}^{HF} + (1 - a)E_{xc}^{PBE} + E_{xc}^{PBE}
\]

(2)

where \( a \) is the mixing coefficient, and \( E_{xc}^{PBE} \) and \( E_{xc}^{PBE} \) are the PBE exchange and correlation energies, respectively.

By eliminating the compensated HF and PBE long-ranged exchange contribution, the following form of \( E_{xc}^{HSE} \) is derived29

\[
E_{xc}^{HSE} = aE_{xc}^{HF,SR}(w) + (1 - a)E_{xc}^{PBE,SR}(w) + E_{xc}^{PBE,LR}(w)
\]

(3)

where LR and SR indicate the long-ranged and short-ranged contributions, respectively, and \( w \) is an adjustable parameter handling the short-ranged interaction. HSE06 uses \( a = 0.25 \) and \( w = 0.2 \). We employ the HSE06 method because this method can provide an accurate result in calculating the electronic structure of the compounds containing the transition-metal elements.26 Especially, HSE06 is an efficient method in describing the bound states because of the local distortion caused by the removal or insertion of a Na ion, whereas the other methods such as GGA and GGA + U might fall.26 As the diffusion of Na ions is affected by the quasiparticle, that is, the so-called small polaron, which forms because of the local distortion, in order to explore accurately the diffusion mechanism of Na ions, the HSE06 method should be employed. The projector augmented-wave method was employed to describe ion–electron interactions.34 A cutoff energy of 400 eV was chosen. A 1 × 2 × 2 k-point mesh was used with respect to the supercell containing four formula units (100 atoms). The convergence condition of the optimization calculations is reached when the residual force was smaller than 0.001 eV/Å.

To reveal the diffusion mechanism inside this material, we first find out the stable magnetic alignments of magnetic ions and correspondingly the most stable configuration of the system. After this, we calculate the optimized geometrical and electronic structures of the most stable configuration. The voltage is derived and compared with the experimental value. The diffusion of Na ion is revealed through the following process: first, the formation of a small polaron accompanying a Na vacancy is explored through the optimization of the defect structure; second, four possible EDPs in which the movement of Na ion is accompanied by the polaron migration are carried out, and the activation energy \( E_a \) of each possible EDP is calculated by using the nudge elastic band method;35 finally, the favorable diffusion pathways in the whole material were explored by combining these EDP processes.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00009.

Magnetic moment alignment of Mn ions in AFM configurations and DOS of the vacancy structure Na2[Mn3(SO4)4]2+ by GGA + U (PDF)

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Notes
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