Ionically Conductive Tunnels in $h$-WO$_3$ Enable High-Rate NH$_4^+$ Storage

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Compared to the commonly applied metallic ion charge carriers (e.g., Li$^+$ and Na$^+$), batteries using nonmetallic charge carriers (e.g., H$^+$ and NH$_4^+$) generally have much faster kinetics and high-rate capability thanks to the small hydrated ionic sizes and nondiffusion control topochemistry. However, the hosts for nonmetallic charge carriers are still limited. In this work, it is suggested that mixed ionic–electronic conductors can serve as a promising host for NH$_4^+$ storage. Using hexagonal tungsten oxide ($h$-WO$_3$) as an example, it is shown that the existence of ionic conductive tunnels greatly promotes the high-rate NH$_4^+$ storage. Specifically, a much higher capacity of 82 mAh g$^{-1}$ at 1 A g$^{-1}$ is achieved on $h$-WO$_3$, in sharp contrast to 14 mAh g$^{-1}$ of monoclinic tungsten oxide (m-WO$_3$). In addition, unlike layered materials, the insertion and desertion of NH$_4^+$ ions are confined within the tunnels of the $h$-WO$_3$, which minimizes the damage to the crystal structure. This leads to outstanding stability of up to 200 000 cycles with 68% capacity retention at a high current of 20 A g$^{-1}$.

1. Introduction

The everlasting energy demands have driven the exponential growth of the battery market, which is currently dominated by Li-ion batteries (LIBs). Other metal-ion batteries (e.g., Na$^+$, K$^+$, Mg$^{2+}$, and Zn$^{2+}$) as alternatives to LIBs are also under rapid development aiming to reduce the cost and improve safety. In contrast, batteries using nonmetallic ions (e.g., H$^+$ and NH$_4^+$) as charge carriers have rarely been explored, although they might have ultrafast kinetics thanks to the small hydrated ionic sizes and nondiffusion control topochemistry. In addition, the use of aqueous electrolytes makes these batteries much safer and cheaper. Proton batteries often use corrosive acidic electrolytes and therefore have a high requirement for materials in the device. On the other hand, batteries using NH$_4^+$ ions as charge carriers have relatively facile operating conditions. To date, only a handful of electrode materials have been investigated for NH$_4^+$ storage, such as Prussian blue analogue with an open framework, Ti$_3$C$_2$ MXene, and V$_2$O$_5$ with layered structures. It is therefore of great interest to explore new materials to further advance the NH$_4^+$ batteries.

The energy storage in NH$_4^+$ batteries is achieved by the simultaneous translocation of NH$_4^+$ ions and electrons. In this regard, mixed ionic–electronic conductors (MIECs) could play an important role in enhancing electrochemical performance. MIECs can conduct both ions and electrons simultaneously, which is more efficient and easier than building two materials that conduct ions and electrons separately. MIECs such as LiCoO$_2$ and LiMnO$_2$ are commonly used as electrodes in LIBs and their properties essentially determine the battery performance. These materials, however, often undergo the transition of crystalline phase upon Li$^+$ insertion/desertion and thus suffer from slow electrode kinetics. Other MIECs include RuO$_2$, H$_2$O, and WO$_3$, whereas the former is highly costly. The stoichiometric WO$_3$ is a semiconductor but could become electronically conductive in its nonstoichiometric form (WO$_3$, $2 < x < 3$) which can be achieved by intercalating a guest ion (e.g., H$^+$) into the WO$_3$ matrix. The WO$_3$-based MIECs have already shown good electrochemical performance toward H$^+$ and Li$^+$ storage and we envision that they would be promising hosts for NH$_4^+$ storage. In this work, we show that the $h$-WO$_3$, whose ionic conduction relies on the water molecules within the tunnels, possesses significantly better NH$_4^+$ storage performance as compared to its polymorph m-WO$_3$. As shown in Figure 1a, the $h$-WO$_3$ consists of six-membered rings that are...
assembled by corner-sharing WO₃ octahedra. The stacking of these rings along with the c-axis forms hexagonal tunnels. These tunnels are filled with water molecules, which serve as ion-conducting chains and therefore promote the transport of NH₄⁺ ions, similar to the biological channels.[20] The water content is around 4.8 wt%, which is determined by thermogravimetric/differential scanning calorimeter (TG/DSC) analysis (Figure S1, Supporting Information). Whereas in m-WO₃, the arrangement of WO₆ is different from that in h-WO₃ and forms a distorted ReO₃-type structure (Figure 1b). [21] Note that there are no water molecules in m-WO₃ structure. Such structural difference results in distinctly different electrochemical behavior of h-WO₃ and m-WO₃, although they are chemically similar. Specifically, the h-WO₃, delivers a high NH₄⁺ storage capacity of 82 mAh g⁻¹ at 1000 mA g⁻¹, whereas only 14 mAh g⁻¹ is achieved on m-WO₃. In addition, the insertion and desorption of NH₄⁺ ions are confined within the tunnels of the h-WO₃, which minimizes the damage to the crystal structure; therefore, high stability is achieved with no significant performance decay for 200 000 cycles even at a high current of 20 A g⁻¹, in sharp contrast to that of m-WO₃, which suffers from fast capacitance drop within only 10 000 cycles. Our work not only provides a new host material for NH₄⁺ ions but also suggests the important role of ionic conducting tunnels in enhancing electrochemical performance.

The h-WO₃ was synthesized by a facile hydrothermal reaction (see details in the Experimental Section). The diffraction peaks (Figure 1c) can be assigned to the hexagonal phase WO₃ (JCPDS #85-2460). After thermal annealing, the h-WO₃ was readily converted to m-WO₃ (JCPDS #43-1035). The phase transformation did not result in significant morphological changes. Both the h-WO₃ (Figure 1d) and m-WO₃ (Figure 1e) show nanorod morphology whereas the latter appears to have a slight aggregation thanks to the thermal treatment. The lattice spacing of 0.31 and 0.26 nm from the HRTEM images can be well indexed to the (200) and (202) planes of h-WO₃ and m-WO₃, respectively. In addition, the h-WO₃ and m-WO₃ flexible electrodes have comparable electron conductivity: 38 and 51 mS cm⁻¹, respectively. The synthesis of morphologically similar nanorods of h-WO₃ and m-WO₃ allows a direct comparison of their electrochemical performance and, therefore, a better understanding of the role of ionic tunnels.

We then tested the NH₄⁺ storage performance of both the h-WO₃ and m-WO₃ using a three-electrode setup, where the h-WO₃ (or m-WO₃) on carbon paper was used as the working electrode, a Ag/AgCl electrode as the reference electrode, and a graphite rod as the counter electrode. In 1 m (NH₄)₂SO₄ electrolyte, the h-WO₃ delivers a high capacity of 82 mAh g⁻¹ at a high current density of 1 A g⁻¹, significantly larger than that of m-WO₃ (14 mAh g⁻¹; Figure 2a). This disparity highlights the vital role of ionic tunnels in enhancing electrochemical performance. The h-WO₃ also possesses a much higher rate capability toward the NH₄⁺ storage in terms of capacity retention at high currents (Figure 2b). For instance, the capacity of h-WO₃ is 20 mAh g⁻¹ at 10 A g⁻¹, whereas it is only 1.3 mAh g⁻¹ for m-WO₃. Besides the high capacity, the h-WO₃ also possesses outstanding stability with an 80% capacity retention at 100 000 cycles and 68% at 200 000 cycles under the current density of 20 A g⁻¹ (Figure 2c). In sharp contrast, the m-WO₃ suffers from quick performance decay within 10 000 cycles. This result indicates the high structural stability of h-WO₃ to readily accommodate NH₄⁺ ions within the tunnels. As shown in Figure S2 (Supporting Information), h-WO₃ has superb cycling performance under medium current density of 5 A g⁻¹ without capacity fading after 5000 cycles. In addition, we also evaluated the electrochemical performance of h-WO₃ for other monovalent metal ions (e.g., Li⁺) storage and found that only a low capacity (17 mAh g⁻¹) was achieved under the same current density (Figure 2a). To better understand the kinetics of these two charge carriers (metal vs nonmetal), simple CV scans at various rates were performed. Figure 2d shows the CV curves of h-WO₃ in 1 m (NH₄)₂SO₄. The redox peaks at −0.15 V versus Ag/AgCl correspond to the intercalation of NH₄⁺ ions into the tunnels. The
As mentioned earlier, the \( \text{h-WO}_3 \) maintains high structural stability because the \( \text{NH}_4^+ \) ions could travel through and be readily accommodated within the ionic tunnels. This is confirmed by the SEM observation that the overall morphology of the \( \text{h-WO}_3 \) does not change upon charging and discharging (Figure 3a; Figure S7, Supporting Information). We further conducted ex situ XRD measurement at selected states of charge. The diffraction peaks generally become broader, indicating that the intercalation of \( \text{NH}_4^+ \) ions reduces the crystallinity of \( \text{h-WO}_3 \) (Figure 3b). In addition, during discharge (corresponding to the \( \text{NH}_4^+ \) insertion process), the peaks shift to a higher degree, which suggests a contraction of the crystal lattice. This could be because the water molecules within the \( \text{h-WO}_3 \) tunnels are partially replaced by the \( \text{NH}_4^+ \) ions with smaller ionic sizes (approximately 2.75 vs. 1.48 Å). Notably, the structure of \( \text{h-WO}_3 \) reversibly expands back upon charging (i.e., \( \text{NH}_4^+ \) desorption). The structural contraction confirms the intercalation of \( \text{NH}_4^+ \) ions into the \( \text{h-WO}_3 \) tunnels and their interactions. The bonding chemistry of \( \text{NH}_4^+ \) ions with \( \text{h-WO}_3 \) host was further demonstrated by the Fourier transform infrared (FTIR) spectra. The IR peak at \( \approx 3189 \text{ cm}^{-1} \) is ascribed to the N–H stretch of a nonbonded H, whereas the one at \( \approx 3010 \text{ cm}^{-1} \) corresponds to the N–H that bonds with the \( \text{h-WO}_3 \) host through H···O bonding (Figure 3c). We noticed that the pristine sample also shows the former peak, which could be due to the preintercalated \( \text{NH}_4^+ \) that was introduced during the synthesis process. The latter peak appears upon discharging and then becomes weakened during charging, which suggests the building and breaking of hydrogen bonds between the \( \text{NH}_4^+ \) and \( \text{h-WO}_3 \) host. In addition, the peak at \( \approx 1080 \text{ cm}^{-1} \) that is ascribed to the \( \text{W=O} \) bond stretches shifts to lower frequency,[25] which is caused by the reversible reduction of \( \text{W}^{6+} \) to \( \text{W}^{5+}/\text{W}^{4+} \).
Figure 3. Study on the NH4+ storage mechanism. a) Charge–discharge profile of h-WO3 in (NH4)2SO4 at 1 A g–1. Ex situ b) XRD, c) FTIR, d) Raman, and e) W 4f XPS characterization of the h-WO3 electrodes at the selected state of charge. The triangle in b marks the diffraction peak from carbon paper substrate.

during the insertion of NH4+ into the h-WO3 framework. The peak intensity and position recover back upon charging and are nearly identical to the initial state, which demonstrates that the insertion and desertion of NH4+ ions are highly reversible. This result was further supported by the Raman analysis (Figure 3d). The characteristic peaks of NH4+ are observed upon discharging. As a result of NH4+ insertion, the W6+ is partially reduced to W5+/W4+. The bonds of W5+/4=O and W5+/4=O are weaker than those involving W6+ ions due to the lower ionic charge, therefore resulting in a redshift of these peaks.[26] The reduction of W6+ to W5+/4 during NH4+ insertion was also revealed by the X-ray photoelectron spectroscopy (XPS) analysis (Figure 3e). The pristine h-WO3 is composed of both the W6+ and W5+ species, suggesting that h-WO3 may contain oxygen vacancies. After the discharge process, W5+ can be identified on the h-WO3 surface, indicating the insertion of NH4+ that causes the reduction of high valent W species. Whereas after charging, the surface oxidation state of W reverses back, again confirming that the NH4+ insertion/desertion is highly reversible and does not induce a significant structural change of the h-WO3 framework. These analyses suggest that the NH4+ ions can reversibly intercalate into and interact with the h-WO3 through the hydrogen bonding chemistry, which enables ultrafast kinetics.

The NH4+ insertion process was further simulated using the density functional theory (DFT) calculations. The lower-energy model structure of NH4+ inserted h-WO3 was first constructed. The energy variation caused by the insertion of one NH4+ ion was −11.32 eV (Table S1, Supporting Information), and the host–guest interaction energy was 2.83 eV for NH4 per bonding, which suggests that the insertion of NH4+ ions would result in distortions of the h-WO3 host. Indeed, the interaction of NH4+ and h-WO3 was found to result in an increase in the W=O bond length from 2.033 to 2.058 Å, which explains the redshifts of the W = O peaks in FTIR and Raman spectra. We also found that the inserted NH4+ interacts with not only the h-WO3 but also the neighboring H2O through the hydrogen bonding (Figure 4a). The building of hydrogen bonds between the NH4+ ions and h-WO3 provides a channel for the electron transfer (2.88 electrons in total) from the oxide to NH4+ as demonstrated by the Bader charge analysis (Figure 4c; Table S2, Supporting Information). As a result, the charge localization is accumulated mostly on the terminal oxygen atoms that are coordinated with NH4+ ions, which benefits the fast charge transfer.[27] We then simulated the transport of NH4+ ions along the ionically conductive tunnels within h-WO3. The NH4+ initially forms three hydrogen bonds with the h-WO3 with an intercalation energy barrier of 0.42 eV (Figure 4b) and then diffuses further into the channel, forming four hydrogen bonds (Figure 4d). Unlike metallic cations such as Li+ that are spherical, the NH4+ has the shape of a regular tetrahedron with four hydrogen atoms located at the vertices at equal distances from the nitrogen center. This configuration allows the NH4+ to twist and rotate during the diffusion to the h-WO3 tunnels. The movement is similar to swinging on monkey bars. As the NH4+ migrates, one of the hydrogen atoms disconnects with the oxygen of the h-WO3 by breaking the hydrogen bonds, and then moves forward to build a new hydrogen bond with the oxygen atom in the front. In contrast, the other three hydrogen atoms remain connected. The breaking and building of hydrogen bonds take place continuously and alternately, which ensures a smooth diffusion of NH4+ into the h-WO3 host and might account for the good rate capability of NH4+. 
We further fabricate an NH4+ full cell with h-WO3 anode and (NH4)0.5V2O5 cathode. (NH4)0.5V2O5 possesses a nanobelt morphology (Figure S9, Supporting Information) with super rate capacity (see Figure S9a,b in the Supporting Information; 57.6 mAh g−1 at 1 A g−1 and cycling stability (see Figure S9c in the Supporting Information; ≈100% capacity retention after 5000 cycles at 5 A g−1). Given the electrochemical performance of (NH4)0.5V2O5 nanobelts, the optimized active mass ratio between cathode and anode should be 1:1. As shown in Figure S9d (Supporting Information), the full cell provides a reversible capacity of about 40 mAh g−1 at 1 A g−1 between 0 and 1.85 V based on the active mass of both electrodes (similarly from now on). The energy density and power density are up to about 34 Wh kg−1 and 4300 W kg−1 (Figure S8e, Supporting Information). Furthermore, the (NH4)0.5V2O5//h-WO3 full cell delivers ultralong cycling stability over 50 000 cycles (capacity retention is about 71%).

In summary, we suggest that the mixed ionic–electronic conductors are promising electrode materials for NH4+ ion batteries. Specifically, we proposed h-WO3 with a hexagonal tunnel structure as a suitable host for NH4+ storage. Thanks to the mixed-ionic–electronic conductivity, the structural stability, and the rich redox reactions, the h-WO3 exhibits high NH4+ storage of 82 mAh g−1 at 1 A g−1 along with outstanding cycled performance up to 200 000 cycles, which are much superior to its polymorph m-WO3 that does not present such ionically conductive tunnels. This work not only establishes the h-WO3 as a promising electrode material for NH4+ ion batteries but also provides insights into the role of mixed ionic–electronic conductivity in enhancing the electrochemical performance of rechargeable batteries that use nonmetallic ions as the charge carriers.

2. Experimental Section

Synthesis of h-WO3 and m-WO3 Nanowires: The h-WO3 nanowires were grown on carbon paper substrate via a hydrothermal reaction.[28] First, 3.8 mmol Na2WO4 ⋅2H2O and 11 mmol H2C2O4 were dissolved in 32 and 48 mL of H2O to form clear solutions, respectively. The pH of the former was adjusted to ≈1 by adding HCl drops before the two solutions were mixed. After that, 15 mmol (NH4)2SO4 was added to the above mixture, which was then transferred to a 100 mL autoclave and heated at 180 °C for 16 h. The carbon paper with h-WO3 nanowires was collected and washed after the reaction. The m-WO3 nanowires were obtained by annealing the h-WO3 nanowires precursor at 500 °C in the air for 3 h. On average, 3.9 mg cm−2 of WO3 nanowires is grown on carbon paper substrate.

Synthesis of (NH4)0.5V2O5 Nanobelts: The (NH4)0.5V2O5 nanobelts were synthesized by one-step hydrothermal method according to previous work.[29] Typically, NH4VO3 (0.29 mg) was dissolved in 35 mL deionized water at 60 °C. Then, β-cyclodextrin (0.34 mg) was added. After continuously stirred for 1 h, H2C2O4 (0.34 mg) was added to the above solution to form a bottle green solution. The solution was then transferred into a 50 mL Teflon-lined autoclave at 120 °C for 10 h. After natural cooling, the products were filtered and washed with deionized water and ethyl alcohol, and then dried at 80 °C for 24 h under vacuum.

Material Characterization: The products were characterized by X-ray diffraction (XRD, Bruker D8 Advance), scanning electron microscopy (SEM, FEI Nova Nano 630), transmission electron microscopy (TEM, FEI Titan CM30), Fourier-transform infrared spectroscopy (FTIR, Nicolet iS10), X-ray photoelectron spectroscopy (XPS, Amicus/ESCA 3400), Raman spectroscopy (LabRAM HR), and TG/DSC (TA STD650).

Electrochemical Measurements: The electrochemical measurements were conducted in a three-electrode cell, where the h-WO3 (or m-WO3) on carbon paper was used as the working electrode, a Ag/AgCl electrode, and a graphite rod were used as the reference electrode and counter electrode, respectively. The electrolyte was either 1 M (NH4)2SO4 or 1 M LiClO4.

Simulations: The present first principle DFT calculations are performed by Vienna Ab initio Simulation Package (VASP)[30] with the projector augmented wave (PAW) method.[31] The exchange-functional is treated using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional.[32] The energy cutoff for the plane wave basis expansion was set to 450 eV and the force on each atom less than 0.01 eV Å−1 was set for the convergence criterion of geometry relaxation. A 1 × 1 × 4 supercell of WO3 was adopted for further simulation. The Brillouin zone integration is performed using 2 × 2 × 1 k-point sampling. The self-consistent calculations apply a convergence energy threshold of 10−5 eV. The DFT-D3 method was employed to consider the van der Waals interaction.[33] Transition state searching was calculated using the climbing-image nudged elastic band (CI-NEB) method.[34] The adsorption energy of NH4+ was calculated according to \( E_{\text{ads}} = (E_{\text{hybrid}} - E_{\text{initial}} - E_{\text{gases}}) \).
$E_{\text{hybrid}} = E_{\text{initial}} + E_{\text{ammonium}} + E_{\text{NH}_4^+}$, where $E_{\text{hybrid}}$ is the total energy of the NH$_4^+$ adsorbed systems, and $E_{\text{initial}}$ and $E_{\text{ammonium}}$ are the energies of the initial WO$_3$ structure and the NH$_4^+$, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

energy storage, ionic tunnels, NH$_4^+$, WO$_3$

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[1] M. Li, J. Lu, Z. Chen, K. Armine, Adv. Mater. 2018, 30, 1800561.
[2] F. Ming, H. Liang, Y. Lei, W. Zhang, H. N. Alshareef, Nano Energy 2018, 53, 11.
[3] J. C. Pramudita, D. Sehrawat, D. Goonetilleke, N. Sharma, Adv. Energy Mater. 2017, 7, 1602911.
[4] R. C. Massé, E. Uchaker, G. Cao, Sci. China Mater. 2015, 58, 715.
[5] H. Liang, Z. Cao, F. Ming, W. Zhang, D. H. Anjum, Y. Cui, L. Cavallo, H. N. Alshareef, Nano Lett. 2019, 19, 3199.
[6] X. Wu, J. J. Hong, W. Shin, L. Ma, T. Liu, X. Bi, Y. Yuan, Y. Qi, T. W. Sutta, W. Huang, J. Neufeind, T. Wu, P. A. Greaney, J. Lu, X. Ji, Nat. Energy 2019, 4, 123.
[7] S. Dong, W. Shin, H. Jiang, X. Wu, Z. Li, J. Holoubek, W. F. Stickle, B. Key, C. Liu, J. Lu, P. A. Greaney, X. Zhang, X. Ji, Chem 2019, 5, 1537.
[8] X. Wu, Y. Qi, J. J. Hong, Z. Li, A. S. Hernandez, X. Ji, Angew. Chem., Int. Ed. 2017, 56, 13026.
[9] C. D. Wessells, S. V. Peddana, M. T. McDowell, R. A. Huggins, Y. Cui, J. Electrochem. Soc. 2011, 159, A98.
[10] M. R. Lukatskaya, O. Mashstatlir, C. E. Ren, Y. Dall’Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, Science 2013, 341, 1502.
[11] J. Janek, Nat. Mater. 2009, 8, 88.
[12] Y. Lin, S. Fang, D. Su, K. S. Brinkman, F. Chen, Nat. Commun. 2015, 6, 6824.
[13] M. M. Thackeray, J. O. Thomas, M. S. Whittingham, MRS Bull. 2000, 25, 39.
[14] Z. Chen, Y. Peng, F. Liu, Z. Le, J. Zhu, G. Shen, D. Zhang, M. Wen, S. Xiao, C.-P. Liu, Nano Lett. 2015, 15, 6802.
[15] D. A. McKeown, P. L. Hagans, L. P. Carette, A. E. Russell, K. E. Swider, D. R. Rolison, J. Phys. Chem. B 1999, 103, 4825.
[16] G. Orsini, V. Tricoli, J. Mater. Chem. 2012, 22, 23861.
[17] H. Zheng, J. Z. Ou, M. S. Strano, R. B. Kaner, A. Mitchell, K. Kalantar-zadeh, Adv. Funct. Mater. 2011, 21, 2175.
[18] O. Bohnke, B. Vuillemien, Mater. Sci. Eng. B 1992, 13, 243.
[19] W.-J. Li, Z.-W. Fu, Appl. Surf. Sci. 2010, 256, 2447.
[20] D. I. Arnon, H. Y. Tsujimoto, G. M.-S. Tang, Proc. Natl. Acad. Sci USA 1981, 78, 2942.
[21] W. Sun, M. T. Yeung, A. T. Lech, C.-W. Lin, C. Lee, T. Li, X. Duan, J. Zhou, R. B. Kaner, Nano Lett. 2015, 15, 4834.
[22] T. Brezesinski, J. Wang, S. H. Tolbert, B. Dunn, Nat. Mater. 2010, 9, 146.
[23] H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt, S.-E. Lindquist, J. Phys. Chem. B 1997, 101, 7117.
[24] A. Zecchina, L. Marchese, S. Bordiga, C. Paze, E. Gianiott, J. Phys. Chem. B 1997, 101, 10128.
[25] V. Brei, O. Melezhyk, S. Prudius, G. Telbiz, O. Oranska, Adsorpt. Sci. Technol. 2005, 23, 109.
[26] S.-H. Lee, H. M. Cheong, C. E. Tracy, A. Mascarenhas, D. K. Benson, S. K. Deb, Electrochim. Acta 1999, 44, 3111.
[27] G. Liang, Y. Wang, Z. Huang, F. Mo, X. Li, Q. Yang, D. Wang, H. Li, S. Chen, C. Zhi, Adv. Mater. 2020, 32, 1907802.
[28] H. Liang, Z. Cao, C. Xia, F. Ming, W. Zhang, A.-H. Emwas, L. Cavallo, H. N. Alshareef, CCS Chem. 2020, 2, 139.
[29] T. He, Y. Ye, H. Li, S. Weng, Q. Zhang, M. Li, T. Liu, J. Cheng, X. Wang, J. Lu, B. Wang, Mater. Today 2021, 43, 53.
[30] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.
[31] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.
[32] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, Phys. Rev. B 1992, 46, 6671.
[33] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[34] G. Henkelman, B. P. Uberuaga, H. Jónsson, J. Chem. Phys. 2000, 113, 9901.