MXenes@Te as a composite material for high-performance aluminum batteries

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ABSTRACT The emerging two-dimensional (2D) materials, MXenes, play an important role in various fields of energy storage and exhibit excellent electrochemical performance. Herein, we prepared few-layered MXenes (F-Ti₃C₂T_x) and loaded Te on the surface of F-Ti₃C₂T_x by using a simple high-temperature evaporation method. In addition, the electrochemical performance of the aluminum battery with F-Ti₃C₂T_x as support material was studied. The initial charge/discharge specific capacities are 987/1096 mA h g⁻¹ at 0.2 A g⁻¹. An obvious discharge voltage plateau of about 1.3 V appears at various current densities. The specific capacity is about 258 mA h g⁻¹ with MXenes@Te as the active material in the aluminum battery, which benefits from the excellent electronic conductivity of the MXenes and their 2D layered structure. Density functional theory calculations were carried out to explore the mechanism. Ti₃C₂O₂@Te is more inclined to adsorb [AlCl₄]⁻ than Ti₃C₂O₂. Furthermore, the valence change behavior of element Te was studied by using thermodynamic calculation (FactSage 7.1). X-ray photoelectron spectroscopy results show that when the battery is fully charged to 2.4 V element Te and Ti ions (Ti³⁺, Ti²⁺) are oxidized to Te⁴⁺ and Ti⁴⁺. In contrast to the charging process, the high-valence Te⁴⁺ and Ti⁴⁺ are reduced again during discharging. Element Te is reduced to lower-valence Te²⁺ when the discharge voltage is lower than 0.6 V, and a higher charge voltage (2.56 V) is required for Te to be oxidized to Te⁶⁺.

Keywords: MXenes@Te, aluminum batteries, specific capacity, density functional theory

INTRODUCTION

The excessive use of fossil fuels has had a significant impact on the environment on which humans depend, which is why researchers around the world have become interested in emerging clean energy [1]. At present, many kinds of emerging energy sources exist, such as solar energy, geothermal energy, hydro energy, wind energy, ocean energy, and chemical energy. However, some problems still need to be addressed regarding the reversible storage and use of energy [2]. With the high reserves (up to 8%), low cost, high safety, and high specific capacity of aluminum, the research on the emerging aluminum battery system has become one of the important directions for

energy storage [3]. In recent years, aluminum batteries based on cathode materials, such as carbon materials [4–8], oxides [9–13], sulfides [14–17], and selenides [18] have been found to exhibit excellent electrochemical performance under normal temperature conditions. However, some challenges remain for the development of aluminum batteries compared with lithium-ion batteries, which is mainly limited by the electrochemical properties of positive electrode materials, such as low capacity and poor cyclic performance [19]. Therefore, finding positive electrode materials with superior electrochemical performance or developing novel aluminum batteries is the key in this field. A rechargeable aluminum–sulfur battery was first reported by Gao *et al.* [20], which demonstrated a capacity of 1000 mA h g⁻¹ for over 20 cycles. In addition, the charge/discharge mechanism was described, and sulfide Al₃S₂ was formed during the charge/discharge processes. Subsequently, Yu *et al.* [21] proposed a rechargeable aluminum–sulfur battery under normal temperature conditions and discussed its charge/discharge mechanism. Similar to lithium–sulfur batteries and sodium–sulfur batteries, a series of polysulfides and sulfides were formed during the charge/discharge processes in aluminum–sulfur batteries. In recent years, aluminum–selenium batteries have also been extensively studied, which deliver excellent electrochemical performance and high discharge voltages of about 1.5 V [22,23]. Most recently, Jiao *et al.* [24] constructed a rechargeable aluminum battery with an initial reversible capacity of 913 mA h g⁻¹, which showed excellent electrochemical performance. Subsequently, a tellurium (Te) nanowire positive electrode was prepared to construct a novel tellurium–aluminum battery, and it delivered an ultra-high discharge capacity of 1026 mA h g⁻¹ at 0.5 A g⁻¹ [25]. The construction of the novel aluminum–tellurium battery has greatly improved the electrochemical performance of aluminum batteries and injects fresh blood into their development. However, few reports have been focused on aluminum–tellurium batteries, and their energy storage mechanism is unclear. The process of inhibiting the shuttle effect of multiple tellurides in particular is cumbersome. Therefore, finding a new host material and studying its compatibility with Te and its electrochemical performance in aluminum batteries are among the research focuses in this field. MXenes are a novel family of two-dimensional (2D) materials first discovered by Gogotsi and co-workers [26,27]. It can be defined with the structural formula of M_{n+1}X_nT_x, where M is a

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transition metal (Ti, V, Cr, Zr, Hf, Nb, Mo, Ta, and W), X is carbon and/or nitrogen, T_x is the terminated functional groups (OH, Cl or F), and n is an integer typically between 1 and 3 [28]. MXenes have numerous kinds of properties (electronic, band gap, layered structure, thermal, and mechanical properties) that play important roles in different fields, especially in energy storage [29,30], such as supercapacitors [31–33], lithium-ion batteries [34–37], sodium-ion batteries [38–41], magnesium-ion batteries [42,43], and lithium–sulfur batteries [44,45]. The lithium–sulfur batteries show excellent electrochemical performance, which benefits from the excellent electronic conductivity of MXenes and their 2D layered structure [46]. Few reports have been made on the application of MXenes in aluminum batteries. In 2017 [47], a rechargeable aluminum battery based on (V_2CT_x) MXenes cathode was reported. The battery's cycling performance is poor, and the cause of the battery capacity decline is still unclear. Subsequently, our laboratory studied the application of MXenes in aluminum batteries and explored their charge/discharge mechanism [48–50]. However, their electrochemical performance in aluminum batteries needs to be improved. Modifying MXenes or combining them with other high-capacity electrode materials is the most effective way to improve its electrochemical performance.

Herein, we used a simple high-temperature evaporation method to load Te on the surface of few-layered MXenes ($F-Ti_3C_2T_x$). The scheme of the preparation is shown in Fig. 1. The microstructure and physicochemical properties of the materials were studied by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). In addition, the electrochemical performance of the aluminum battery with MXene as the support material was studied, which exhibited excellent rate performance and cyclic stability. Furthermore, density functional theory (DFT) calculations were performed to explore the mechanism, and the valence change behaviors of Te and Ti ions were studied by thermodynamic calculation (FactSage 7.1) and X-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

As shown in Fig. 2a, the pattern of Ti_3AlC_2 (purchased from 11 Tech.) shows two distinct characteristic peaks (002) and (104). After etching with HF acid, the peak (104) completely disappeared, and the peak (002) moved from 9.52° to 8.98° , even lower angles, which indicated that Al was removed by HF acid, and the 2D $Ti_3C_2T_x$ was prepared [51]. Furthermore, the prepared $Ti_3C_2T_x$ was ultrasonically stripped in ethanol, and the

peak (002) moved from 8.98° to 7.08° (Fig. 2a), indicating that the lattice spacing of the peak (002) increased [52]. Fig. 2b shows the XRD patterns of $Ti_3C_2T_x$ and $F-Ti_3C_2T_x@Te$. The electrode materials $Ti_3C_2T_x@Te$ and $F-Ti_3C_2T_x@Te$ show obvious characteristic peaks of Te, indicating that a large amount of Te is loaded on the surface of the materials [45]. As shown in Fig. 2c, d, the XPS spectra of Ti 2p in $F-Ti_3C_2T_x$ and $F-Ti_3C_2T_x@Te$ indicate that the Ti bonds on the surface of $F-Ti_3C_2T_x$ changed after Te loading. During the process of Te loading, low-valence Ti ions were oxidized to higher-valence Ti^{4+} , which improved the stability of $F-Ti_3C_2T_x@Te$ [48]. Fig. 2e shows the N_2 adsorption/desorption isotherm plots of $Ti_3C_2T_x$ and $F-Ti_3C_2T_x$. The specific surface areas of $Ti_3C_2T_x$ and $F-Ti_3C_2T_x$ are 11.5 and $32.7\text{ m}^2\text{ g}^{-1}$, respectively. Fig. 2f shows the pore size distributions of $Ti_3C_2T_x$ and $F-Ti_3C_2T_x$. Some micropores with a size of 3.5 nm appear in $F-Ti_3C_2T_x$. The specific surface area changes from 11.5 to $32.7\text{ m}^2\text{ g}^{-1}$, and some micropores appear inside $F-Ti_3C_2T_x$. As shown in Fig. 2g, $Ti_3C_2T_x@Te$ presents a strong endothermic peak at $500\text{--}650^\circ\text{C}$ with the peak temperature around 620°C , and the mass percentage of Te is approximately 49.8%. As shown in Fig. 2h, $F-Ti_3C_2T_x@Te$ also shows a strong endothermic peak at $500\text{--}650^\circ\text{C}$. However, its peak temperature drops slightly to about 608°C , indicating that Te escapes from $F-Ti_3C_2T_x@Te$ more easily. In addition, the TGA curve (Fig. 2h) still shows a downward trend between $650^\circ\text{C}\text{--}800^\circ\text{C}$, which may be due to some Te entering the mesopores of the MXenes during the high-temperature evaporation process, and the mass ratio of Te is about 57.3%. Physicochemical characterizations show that the MXenes@Te composite was successfully prepared, and the MXenes loaded more elemental Te after stripping.

The microscopic morphology of the materials was further characterized by SEM and TEM. The Ti_3AlC_2 shows a 3D block structure (Fig. 3a) before etching. The $Ti_3C_2T_x$ exhibits a uniform 2D layered structure after etching by HF acid, and the thickness of one single layer is less than 1 nm (Fig. 3b, c). The Al in Ti_3AlC_2 is selectively removed by HF acid. After the Al atomic layer is lost, the 3D (MAX) material Ti_3AlC_2 is transformed into the 2D (MXene) material $Ti_3C_2T_x$. The atomic structure before and after etching is shown in Fig. S1. The SEM image of $F-Ti_3C_2T_x$ is shown in Fig. 3d, and the multilayered $Ti_3C_2T_x$ changed into $F-Ti_3C_2T_x$ after stripping. The specific surface area of $F-Ti_3C_2T_x$ becomes larger as shown in the microscopic perspective, which is consistent with the N_2 desorption/adsorption tests (Fig. 2c). Fig. 3e shows the TEM image of $Ti_3C_2T_x$. The microstructure of $Ti_3C_2T_x$ is 2D with multilayer stacking, and each single layer is composed of many thinner layer stacks.

Figure 1 Schematic illustration of the synthesis of MXenes@Te.

Figure 2 XRD patterns of (a) Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{F-Ti}_3\text{C}_2\text{T}_x$, (b) $\text{Ti}_3\text{C}_2\text{T}_x@Te$ and $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$. (c, d) XPS spectra of Ti 2p in $\text{F-Ti}_3\text{C}_2\text{T}_x$ and $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$. (e) N_2 adsorption/desorption isotherm plots of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{F-Ti}_3\text{C}_2\text{T}_x$. (f) The micropore size distributions of $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{F-Ti}_3\text{C}_2\text{T}_x$, calculated with the Barrett-Joyner-Halenda (BJH) method. TGA profiles of (g) $\text{Ti}_3\text{C}_2\text{T}_x@Te$ and (h) $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$.

Fig. 3f shows the TEM image of $\text{F-Ti}_3\text{C}_2\text{T}_x$, which presents a sheet structure with a size of about 500 nm. Fig. 3g shows the SEM image of $\text{Ti}_3\text{C}_2\text{T}_x@Te$, and Te is adsorbed on the surface and the interlayer of $\text{Ti}_3\text{C}_2\text{T}_x$. The $\text{Ti}_3\text{C}_2\text{T}_x@Te$ presents a 3D block structure, and the introduction of Te blocks the channels between the layers of $\text{Ti}_3\text{C}_2\text{T}_x$. In Fig. 3h, the SEM image of $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$ shows that Te is uniformly adsorbed on the surface of $\text{F-Ti}_3\text{C}_2\text{T}_x$. Therefore, effective delamination is essential to the Te loading, thereby avoiding the agglomeration of Te on the surface of $\text{F-Ti}_3\text{C}_2\text{T}_x$ [53]. Fig. 3i shows the energy-dispersive X-ray spectrometer (EDS) surface scans of $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$, which is mainly composed of C, Ti, and Te elements. Fig. S2 shows the EDS spectrum of $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$, which is mainly composed of C, Ti, and Te elements, and a small amount of O and F elements come from the functional groups on the surface [54]. The EDS surface scans of $\text{Ti}_3\text{C}_2\text{T}_x@Te$ are shown in Fig. S3. According to the characterization of SEM and TEM, effective delamination is important for Te loading, and the Te loading on $\text{F-Ti}_3\text{C}_2\text{T}_x$ surface is more uniform.

Subsequently, the electrochemical performances of $\text{Ti}_3\text{C}_2\text{T}_x@Te$ and $\text{F-Ti}_3\text{C}_2\text{T}_x@Te$ were studied in aluminum batteries. Fig. S4 shows the electrochemical performance of

$\text{Ti}_3\text{C}_2\text{T}_x@Te$ in aluminum batteries. Fig. S4a shows the cyclic voltammetry (CV) curve with a scan rate of 0.5 mV s^{-1} and a scan range of 0.01–2.4 V. The open circuit voltage of the aluminum battery is about 1.5 V. Obvious cathode peaks are around 0.5, 2.0, and 2.2 V, and obvious anode peaks are located around 1.3, 1.0, and 0.4 V. Fig. S4b shows the charge/discharge curves at different current densities, consistent with the CV curves. When the current density is 0.2 A g^{-1} , the charge specific capacity is 1121 mA h g^{-1} (Te as the active material), and the discharge specific capacity is 1186 mA h g^{-1} . When the current densities are set to 0.4, 0.6, 0.8, 1.0, and 1.5 A g^{-1} , the discharge specific capacities are 446, 375, 304, 239, and 212 mA h g^{-1} , respectively. As shown in Fig. S4c, the charge/discharge capacities gradually decrease in steps when the current density increases from small to large. The discharge specific capacity is about 200 mA h g^{-1} at a current density of 1.5 A g^{-1} , indicating an excellent rate performance. Fig. S4d shows the cycling performance, and the discharge specific capacity is 275 mA h g^{-1} with a current density of 0.6 A g^{-1} after 150 cycles. The coulombic efficiency is close to 100% during the cycle. However, the capacity retention rate is only about 45% because the multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ causes the reunion of the loaded Te [55]. Therefore, the cyclic stability

Figure 3 SEM and TEM images of the samples. SEM images of (a) Ti_3AlC_2 , (b, c) $\text{Ti}_3\text{C}_2\text{T}_x$, (d) $\text{F-Ti}_3\text{C}_2\text{T}_x$; TEM images of (e) $\text{Ti}_3\text{C}_2\text{T}_x$, (f) $\text{F-Ti}_3\text{C}_2\text{T}_x$; SEM images of (g) $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ and (h) $\text{F-Ti}_3\text{C}_2\text{T}_x@\text{Te}$; (i) selected scan area of $\text{F-Ti}_3\text{C}_2\text{T}_x@\text{Te}$.

needs to be improved.

Fig. 4 shows the electrochemical performance of the aluminum battery with $\text{F-Ti}_3\text{C}_2\text{T}_x$ as the support material. Fig. 4a presents the CV curves with a scan rate of 0.5 mV s^{-1} and a scan range of 0.01–2.4 V. To better explain the redox reaction, we conducted two cycles of CV test on the battery. The CV curves are almost the same with obvious cathode peaks around 0.5, 1.0, 1.4, 2.0, and 2.3 V and obvious anode peaks around 1.3, 1.0, 0.8, and 0.4 V. We conducted a CV test with a tantalum sheet as the cathode and an aluminum sheet as the anode to prove its stability in aluminum batteries. The test results reveal that it does not undergo a strong oxidation reaction under high voltage (2.4 V) conditions. Fig. 4b shows the initial and second charge/discharge curves, and the inset is the curve of the voltage *versus* time during the charge/discharge processes. The initial charge specific capacity is 987 mA h g^{-1} , and the discharge specific capacity is 1096 mA h g^{-1} . Two charge platforms are present around 2.0 and 2.3 V when charged from the open circuit voltage (1.4 V) first, and two discharge platforms are present around 1.3 and 1.0 V during discharging. In addition, two short discharge platforms appear around 0.8 and 0.5 V. The charge specific capacity for the second cycle is 1377 mA h g^{-1} , and the discharge specific capacity is 1365 mA h g^{-1} . The charge curve shows three small charge platforms at about 0.5, 1.0, and 1.3 V. The discharge voltage platform is slightly higher than that of the initial value, and the charge/discharge specific capacities are higher than the initial ones, probably because the initial charge starts from the open circuit voltage (1.4 V), and Te is not sufficiently oxidized. Fig. 4c, d show the charge/discharge curves and rate performance of the aluminum batteries under different

current density conditions. As shown in Fig. 4d, when the current density increases from small to large, the charge/discharge capacities decrease in a stepwise manner. When the current is 1.5 A g^{-1} , the specific capacity is about 400 mA h g^{-1} , and when the current density is reset to 0.6 A g^{-1} , the charge/discharge capacities show a steadily increasing trend in steps. Fig. 4e shows the cyclic stability of the aluminum battery. When the current density is 0.6 A g^{-1} , the discharge specific capacity is 449 mA h g^{-1} after 150 cycles (Te as the active material). The capacity retention rate is about 70%, and the coulombic efficiency is close to 100%. Although the aluminum batteries with $\text{F-Ti}_3\text{C}_2\text{T}_x$ and $\text{F-Ti}_3\text{C}_2\text{T}_x$ as support materials are not inferior in terms of rate performance, the cycling performance of $\text{F-Ti}_3\text{C}_2\text{T}_x@\text{Te}$ in aluminum batteries is much better than that of $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ [53]. In addition, the cycling performance of $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ in aluminum battery is unstable due to the rearrangement of Te during the charge/discharge processes. Furthermore, we studied the self-discharge behavior of $\text{F-Ti}_3\text{C}_2\text{T}_x@\text{Te}$ in aluminum batteries and showed the charge/discharge curves after different cycles. As shown in Fig. 4f, the prepared new battery was charged to 2.4 V after 4 h of rest, and the voltage was instantly reduced from 2.4 to 1.57 V after charging. After 48 h of rest, the voltage of the aluminum battery almost did not change significantly, and the final voltage was slightly higher than the open circuit voltage (1.4 V). The above results clearly show that the electrode material is stable in the electrolyte without a strong self-discharge behavior. Fig. 4g shows the charge/discharge curves after different cycles at a current density of 0.6 A g^{-1} .

The electrochemical performances of $\text{F-Ti}_3\text{C}_2\text{T}_x$ and Te were studied in aluminum batteries to distinguish the capacities

Figure 4 (a) CV curves of F-Ti₃C₂T_x@Te. (b) Charge/discharge curves of F-Ti₃C₂T_x@Te at 0.2 A g⁻¹. (c, d) Rate performance of F-Ti₃C₂T_x@Te. (e) Cycling performance and coulombic efficiency of F-Ti₃C₂T_x@Te at 0.6 A g⁻¹. (f) Self-discharge behavior of the battery. (g) Charge/discharge curves of F-Ti₃C₂T_x@Te after different cycles. (h) Cycling performances of F-Ti₃C₂T_x, Te, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te. (i) Alternative current (AC) impedance spectra of F-Ti₃C₂T_x, Te, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te.

provided by the support materials F-Ti₃C₂T_x and Te. Fig. S5 shows the electrochemical performance of F-Ti₃C₂T_x in aluminum batteries. As shown in Fig. S5a, the CV curve presents obvious anode peaks around 1.0 and 0.5 V. Fig. S5b shows the initial and second charge/discharge curves, consistent with the CV curve. When the current density is 0.6 A g⁻¹, the initial charge specific capacity is 153 mA h g⁻¹, and the discharge specific capacity is 164 mA h g⁻¹ with a discharge platform around 1.0 V. The charge specific capacity for the second cycle is 113 mA h g⁻¹, and the discharge specific capacity is 89 mA h g⁻¹. Fig. S5c shows the rate performance of F-Ti₃C₂T_x in the aluminum battery. The specific capacity is about 30 mA h g⁻¹ at 1.5 A g⁻¹ and is approximately 50 mA h g⁻¹ at the current density of 0.6 A g⁻¹. Fig. S5d shows the cyclic stability. When the current density is 0.6 A g⁻¹, the specific capacity is stable between 50–60 mA h g⁻¹ during 150 cycles. F-Ti₃C₂T_x shows excellent rate performance in aluminum batteries because of the good conductivity of MXenes. However, when the current density is set to 0.6 A g⁻¹, the stable capacity provided by F-Ti₃C₂T_x in aluminum batteries is less than 60 mA h g⁻¹. Fig. S6 shows the electrochemical performance of Te in aluminum batteries, and Fig. S6a shows the CV curve for the initial and second cycles. Obvious cathode peaks are around 0.5, 1.0, and 2.3 V, and a continuous

anode peak is around 1.5 V, which correspond to the charge/discharge curves (Fig. S6b). The charge specific capacity of Te is 516 mA h g⁻¹ in aluminum batteries, and the discharge specific capacity is 678 mA h g⁻¹ (current density of 0.6 A g⁻¹). Fig. S6c shows the cyclic stability, and the specific capacity is 95 mA h g⁻¹ after 110 cycles with a current density of 0.6 A g⁻¹. The specific capacity of Te decays severely in the aluminum battery. Fig. 4h shows the cyclic stabilities of F-Ti₃C₂T_x, Te, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te in aluminum batteries. The aluminum battery with F-Ti₃C₂T_x@Te as the cathode material has the best cyclic stability during 150 cycles at a current density of 0.6 A g⁻¹, and the specific capacity is about 258 mA h g⁻¹ after 150 cycles (F-Ti₃C₂T_x@Te as the active material). Fig. 4i shows the impedance spectra of Te, F-Ti₃C₂T_x, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te in aluminum batteries, respectively. Obviously, they are composed of two semi-circles (high-frequency region) and one upward sloping line (low-frequency region). The data obtained by fitting the equivalent circuit diagram (inset in Fig. 4i) are shown in Table S1. The Ohmic impedances R_s of Te, F-Ti₃C₂T_x, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te in aluminum batteries are about 50 Ω, which have no close relationship with the cathode materials. R_{sf} is the impedance of solid electrolyte interface (SEI) film at the interface of the electrode material, and R_{ct} is the charge

transfer impedance. The charge transfer impedances R_{ct} of Te, F-Ti₃C₂T_x, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te in aluminum batteries are 138, 98, 121, and 102 Ω , respectively. The interface impedances R_{sf} of Te, F-Ti₃C₂T_x, Ti₃C₂T_x@Te, and F-Ti₃C₂T_x@Te in aluminum batteries are 432, 176, 326, and 240 Ω , respectively. The fitted data show that the R_{ct} and R_{sf} of Te in aluminum batteries are high, which is determined by its nature of semi-conducting. The R_{ct} and R_{sf} of F-Ti₃C₂T_x@Te in aluminum batteries are 102 and 240 Ω , respectively. Compared with those of Te electrodes, they are significantly reduced, because MXenes have excellent electrical conductivity. In addition, the modified F-Ti₃C₂T_x contains more micropores, which can better promote the transfer of electrons and charges [56].

The Te element belongs to the oxygen group elements and exhibits different valence states (Te^{2-} , Te^{2+} , Te^{4+} , and Te^{6+}) when oxidized or reduced. Herein, we studied the charge/discharge mechanism by using electrochemical methods, thermodynamic calculations (FactSage 7.1), and XPS characterization. Fig. 5a shows the CV curve of the aluminum battery with F-Ti₃C₂T_x@Te as the cathode material. The curve starts from the open circuit voltage of 1.4 V; the pink curve is the initial cycle, and the green curve is part of the second cycle. The entire cycle process is divided into three parts: I, II, and III. The charge/discharge mechanism is shown in the following chemical equations. Equation (1) represents the chemical reaction occurring in part I, Equation (2) is the chemical reaction occurring in part II, and Equations (3 and 4) are the chemical reactions occurring in part III. All the above chemical reactions take place at the cathode of the aluminum battery. Equation (5) is the chemical reaction that takes place at the anode of the aluminum battery. Furthermore, we calculated the potentials (vs. Al/Al³⁺) when Te was oxidized or reduced to different valence states by using thermodynamic software (FactSage 7.1). The calculated results are shown in Table S2. When Te is reduced to Te^{2-} , the potential is 0.65 V. When Te is oxidized to Te^{2+} , Te^{3+} , Te^{4+} , and Te^{6+} , the potentials are 1.36, 2.60, 1.56, and 2.57 V, respectively. The potential is 1.76 V when Te^{2+} is oxidized to TeCl_3^+ [24,25,57]. Therefore, we conclude that Te is oxidized to Te^{2+} and Te^{4+} during the charge process of 1.4–2.4 V. The high-valence Te^{4+} is gradually reduced to Te in the discharge process of 2.4–0.01 V, and Te is reduced to Te^{2-} as the voltage decreases.

Cathode:

I

II

III

Anode:

Fig. 5b shows the charge/discharge curves, and the charge/discharge platforms (2.2–2.4, 1.4–1.2, 1.2–0.9, 0.9–0.3, 0.5–1.1, 1.1–1.5 and 1.5–2.2 V) marked in the curve correspond to the redox peaks of the CV curve. The specific capacity is 987 mA h g⁻¹ (the theoretical specific capacity of Te– Te^{4+} is

844.2 mA h g⁻¹) when the battery is charged from the open circuit voltage (approximately 1.4 V) to 2.4 V at the current density of 0.2 A g⁻¹. When the battery is discharged to 1.2, 0.9, and 0.3 V under the current density of 0.2 A g⁻¹, the discharge specific capacities are 303, 652, and 756 mA h g⁻¹, respectively. When the battery is charged from 0.01 to 1.1, 1.5 and 2.2 V under the current density of 0.2 A g⁻¹, the charge specific capacities are 100, 170, and 651 mA h g⁻¹, respectively. The charge/discharge specific capacity of each stage is closely related to the redox reactions of Te. However, because the valence state change behavior of Te is continuous during the charge/discharge processes, the division of the specific capacities in the above stages does not completely match the valence change behavior of Te [24]. Fig. 5c shows the charge/discharge curves with a current density of 0.2 A g⁻¹. The initial discharge specific capacity is 256 mA h g⁻¹ (the theoretical specific capacity of Te– Te^{2-} is 422.1 mA h g⁻¹), and the charge specific capacity is 1152 mA h g⁻¹ (the theoretical specific capacity of Te^{2-} – Te^{4+} is 1266.4 mA h g⁻¹). The actual test capacities are lower than the theoretical specific capacities, which may be due to the chemical dissolution of Te. In addition, many factors need to be controlled to achieve the theoretical specific capacity of the active material in actual experiments, such as current density, battery assembly process, and electrolyte. As shown in Fig. S7, the electrolyte is purple after cycling (Fig. S7a). However, the composite material F-Ti₃C₂T_x@Te can exist in the electrolyte stably (Fig. S7b).

In addition, we performed XPS characterization on F-Ti₃C₂T_x@Te under different voltage conditions to determine the valence change behavior of Te during charging/discharging. Fig. 5d shows the XPS spectrum of Te when fully charged to 2.4 V from 1.4 V (open circuit voltage). The binding energy peaks at 576.5 and 587.2 eV are assigned to Te 3d_{3/2} and Te 3d_{5/2} of Te^{4+} , respectively, indicating that Te is almost completely oxidized to Te^{4+} after full charging to 2.4 V. Fig. 5e shows the XPS spectrum of Te when discharged from 2.4 to 1.2 V. The binding energy peaks at 576.5 and 587.2 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te^{4+} , respectively, and the binding energy peaks at 573.0 and 583.7 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te [58], respectively, indicating that the high-valence Te^{4+} begins to be reduced to Te during the discharge process. Fig. 5f is the XPS spectrum of Te when discharged to 0.9 V. The binding energy peaks at 575.3 and 586.2 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te^{2+} , respectively, and the peaks at 573.0 and 583.7 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te, respectively. As the discharge process progresses, Te^{4+} is reduced to Te^{2+} and Te. Fig. 5g presents the XPS spectrum of Te when discharged to 0.3 V. The peaks at 575.3 and 586.2 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te^{2+} , respectively, and the peaks at 572.4 and 582.7 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te^{2-} , respectively. When the voltage is 0.3 V, Te^{4+} begins to be reduced to Te^{2+} and Te^{2-} . Fig. 5h–j shows the valence change behavior of Te during charging. Corresponding to the discharge process, when the battery is charged to 1.1 V, the peaks at 575.3 and 586.2 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te^{2+} , respectively, and the peaks at 573.0 and 583.7 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te, respectively. When the battery is charged to 1.5 and 2.2 V, the peaks at 575.3 and 586.2 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te^{2+} , respectively, and the peaks at 576.5 and 587.2 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te^{4+} , respectively. The specific parameter is shown in Table S3, and the low-valence Te ions are oxidized to a high-valence state during the charge process. Consistent with the theoretical cal-

Figure 5 Electrochemical performance of F-Ti₃C₂T_x@Te in aluminum battery. (a) CV curves, (b) charge/discharge curves, and (c) charge/discharge curve (discharge first). XPS spectra of Te under different voltage conditions: (d) charged to 2.4 V, (e) discharged to 1.2 V, (f) discharged to 0.9 V, (g) discharged to 0.3 V, (h) charged to 1.1 V, (i) charged to 1.5 V, (j) charged to 2.2 V, and (k) discharged to 0.01 V.

culations, the valence change behavior of Te provides capacity for aluminum batteries during charging/discharging. Fig. 5k provides the XPS spectrum of Te when the battery is directly discharged to 0.01 V. The peaks at 572.4 and 582.7 eV are those of Te 3d_{3/2} and Te 3d_{5/2} of Te²⁺, respectively, and the peaks at 575.3 and 586.2 eV belong to Te 3d_{3/2} and Te 3d_{5/2} of Te⁴⁺ [24], respectively, indicating that Te can be reduced to Te²⁺ at a low

potential. A small amount of Te²⁺ may come from the chemical dissolution of Te in the electrolyte.

The charge/discharge mechanism of the host material F-Ti₃C₂T_x in aluminum batteries was studied by XPS, and the XPS spectra of Ti 2p, Cl 2p, and Al 2p under different voltages are shown in Fig. S8. Fig. S8a–d depict the valence change behavior of Ti ions during charging/discharging. The Ti ions on the

Figure 6 Result of DFT calculations for (a) adsorption of $[\text{AlCl}_4]^-$ by $\text{Ti}_3\text{C}_2\text{O}_2$; (b) models of the interaction of Te and $\text{Ti}_3\text{C}_2\text{O}_2$; (c) adsorption of $[\text{AlCl}_4]^-$ by Te; (d) adsorption of $[\text{AlCl}_4]^-$ by $\text{Ti}_3\text{C}_2\text{O}_2@\text{Te}$.

surface of the material are oxidized to a high-valence state (Ti^{4+}) during charging, and the high-valence Ti ions are reduced to a low-valence state (Ti^{3+} , Ti^{2+}) again during the discharge process. The specific data are shown in Table S4. In the aluminum batteries, the percentage of Ti^{4+} before charging/discharging, fully charged to 2.4 V, and discharged to 0.01 V is 11.8%, 26.9%, and 14.6%, respectively. The valence behavior of Ti-ions provides a certain capacity. Fig. S8e, f depict the XPS spectra of Al 2p and Cl 2p under different voltage conditions. When F- $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ is fully charged to 2.4 V in an aluminum battery, it shows obvious characteristic peaks of Cl 2p and Al 2p. The intensity of the characteristic peak Cl 2p and Al 2p weakens during discharging. F- $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ shows weak characteristic peaks of Cl 2p and Al 2p when fully discharged to 0.01 V, illustrating that the $[\text{AlCl}_4]^-$ carrying Cl is deintercalated from F- $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$. This finding is consistent with the valence behavior of Te, and the intercalation/deintercalation of $[\text{AlCl}_4]^-$ caused the valence behaviors of Te and Ti ions. The reaction process is shown in Equations (6 and 7).

Cathode:

Anode:

DFT calculations were performed to explore the mechanism. First-principles calculations were carried out in the DFT framework, as implemented in the Vienna *ab initio* simulation package [59,60]. The binding energy (E_{binding}) was calculated as Equation (8):

$$E_{\text{Binding}} = E_{(\text{MXene}+[\text{AlCl}_4]^-)} - (E_{\text{MXene}} + E_{[\text{AlCl}_4]^-}). \quad (8)$$

The DFT calculation results are shown in Fig. 6. Fig. 6a shows the adsorption between $[\text{AlCl}_4]^-$ and $\text{Ti}_3\text{C}_2\text{O}_2$, and the adsorption energy is -1.19 eV . Fig. 6b presents the models of the interaction of Te and $\text{Ti}_3\text{C}_2\text{T}_x$. Three ways are used to combine Te with $\text{Ti}_3\text{C}_2\text{T}_x$. When Te is combined with C bond, functional group $-\text{OH}$, and Ti bond, the binding energies are -592.6 , -593.0 , and -592.7 eV , respectively. The calculation shows that Te is most stable when combined with the functional group $-\text{OH}$. Therefore, the most stable $\text{Ti}_3\text{C}_2\text{O}_2@\text{Te}$ is used to establish a model to calculate the adsorption energy with $[\text{AlCl}_4]^-$. As shown in Fig. 6c, the adsorption energy between $[\text{AlCl}_4]^-$ and

$\text{Ti}_3\text{C}_2\text{O}_2@\text{Te}$ is -2.82 eV , which indicates that $\text{Ti}_3\text{C}_2\text{O}_2@\text{Te}$ is more inclined to adsorb $[\text{AlCl}_4]^-$ than $\text{Ti}_3\text{C}_2\text{O}_2$. Fig. 6d shows the adsorption between $[\text{AlCl}_4]^-$ and Te, and the adsorption energy is -2.83 eV . Although Te can also adsorb $[\text{AlCl}_4]^-$ stably, the electrochemical performance is poor in the absence of F- $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. S6).

CONCLUSIONS

In summary, the electrochemical performance of the aluminum battery with MXenes as the support material was studied. The battery shows excellent electrochemical performance, and it has an initial charge specific capacity of 987 mA h g^{-1} at 0.2 A g^{-1} and a discharge specific capacity of 1096 mA h g^{-1} with an obvious discharge platform around 1.3 V . The specific capacity is 449 mA h g^{-1} after 150 cycles with a current density of 0.6 A g^{-1} , and the capacity retention rate is about 70%. Furthermore, the valence behaviors of Te and Ti ions were studied. Te and Ti ions (Ti^{3+} , Ti^{2+}) are oxidized to Te^{4+} and Ti^{4+} when the battery is fully charged to 2.4 V, and the high-valence Te^{4+} and Ti^{4+} are restored to Te and Ti ions (Ti^{3+} , Ti^{2+}) during discharging. Te is reduced to lower-valence Te^{2-} when the discharge voltage is lower than 0.6 V in the aluminum battery. In addition, the $[\text{AlCl}_4]^-$ intercalation/deintercalation into F- $\text{Ti}_3\text{C}_2\text{T}_x@\text{Te}$ is proved, and the intercalation/deintercalation of $[\text{AlCl}_4]^-$ causes the valence behaviors of Te and Ti ions.

Aluminum batteries with a higher specific capacity are expected to be prepared due to the multivalence state of Te. However, some challenges in preparing aluminum batteries remain due to the strongly acidity of the electrolyte and the metal properties of Te. First, the electrolyte of the aluminum battery should be improved to reduce the chemical dissolution of Te. Second, the electrode material and separator should be further modified to suppress the shuttle effect of Te. Considering their outstanding advantages of safety and low price, rechargeable aqueous aluminum batteries are also an important research direction [61,62].

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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MXenes@Te作为高性能铝电池复合正极材料

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摘要 新兴的二维材料MXenes在储能领域中发挥着重要作用,并展现了优异的电化学性能。本文中我们制备了二维层状MXenes ($\text{F-Ti}_3\text{C}_2\text{T}_x$),通过高温蒸镀法将Te单质负载在 $\text{F-Ti}_3\text{C}_2\text{T}_x$ 的表面,以MXenes@Te作为铝电池正极,其首次充/放电比容量为 $987/1096 \text{ mA h g}^{-1}$ 。在不同电流密度条件下,铝电池的放电电压平台稳定在1.3 V左右,当以MXenes@Te为活性材料计算时,铝电池的比容量为 258 mA h g^{-1} ,这得益于MXenes材料优异的电导率及其二维层状结构。通过密度泛函理论探索了其机理,计算结果表明, $\text{Ti}_3\text{C}_2\text{O}_2\text{@Te}$ 比 $\text{Ti}_3\text{C}_2\text{O}_2$ 更倾向于吸附 $[\text{AlCl}_4]^-$ 。此外,通过热力学计算(Factsage7.1)和X射线光电子能谱研究了元素Te的价态变化。研究表明,当铝电池充满至2.4 V时,单质Te和Ti离子(Ti^{3+} , Ti^{2+})被氧化为 Te^{4+} 和 Ti^{4+} 。在放电过程中,高价态的 Te^{4+} 和 Ti^{4+} 被重新还原为单质Te和Ti离子(Ti^{3+} , Ti^{2+})。当放电电压低于0.6 V时,单质Te被还原为更低价态的 Te^{2-} ,而要将单质Te氧化为 Te^{6+} ,则需要更高的充电电压(2.56 V)。