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Abstract

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Electrochemical Potassium/Lithium-ion Intercalation into TiSe_2 : Kinetics and Mechanism

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Abstract: As one promising candidate for next-generation energy storage systems, K-ion batteries (KIBs) attract increasing research attention due to the element abundance, low cost, and competent energy density as compared to Li-ion batteries. However, developing practical electrode materials in particular cathodes for KIBs is still in its infancy, and the related reaction mechanisms of the electrode materials are far from completely understood. In this work, TiSe_2 was, for the first time, investigated as an intercalated-type electrode for potassium storage due to its large interlayer space. The potassiation/depotassiation reaction mechanism was unraveled based on the analysis of *in-situ* X-ray diffraction (XRD), *ex-situ* X-ray photoelectron spectroscopy (XPS), and *ex-situ* transmission electron microscope (TEM) results. Meanwhile, the lithium storage behaviour and the relevant lithiation/delithiation reaction mechanism were also studied in detail. The results reveal that K^+ show lower diffusion coefficient and hence more sluggish intercalation reaction kinetics as compared with Li^+ . In addition, the intercalation reaction of K^+ would cause irreversible structure changes, while the intercalation reaction is fully reversible for Li^+ counterpart.

Keywords: TiSe_2 , K-ion batteries, Li-ion batteries, reaction mechanism, diffusion kinetics

1. Introduction

Currently, Li-ion batteries (LIBs) dominate the market of portable electronic devices and are extending their applications in electric vehicles and renewable energy storage due to their

high energy density and power density. [1, 2] However, the scarcity of lithium resources in Earth's crust and the high extraction cost will inevitably restrict its long-term applications. [3, 4] Hence, increasing attention has been transferred to Na-ion batteries due to the cost-effective, natural abundance of sodium resources, and chemical similarity with Li-ion batteries. [5, 6] Unfortunately, Na-ion batteries possess relative low energy density because the standard electrode potential of Na^+/Na (-2.714 V vs. SHE) is 300 mV higher than that of Li^+/Li (-3.040 V vs. SHE), which limits their potential industrial applications. [6, 7] Recently, potassium-ion batteries (KIBs) has emerged as one promising alternative to LIBs based on their unique properties. [8] Firstly, the standard electrode potential of K^+/K (-2.936 V vs. SHE) is 220 mV lower than Na counterpart, which contributes to wider electrochemical voltage window and improved energy density for KIBs. [4, 9] In electrolyte system, the standard potential of K^+/K could exhibit more negative than that of Li^+/Li . Here is an example that K^+/K potential is -0.15 V vs Li^+/Li reference in ethylene carbonate/diethyl carbonate (EC/DEC) electrolyte, indicating its advantage in non-aqueous medium compared to LIBs. [4, 8] Secondly, potassium resources (2.09 wt %) are also much abundant than lithium (0.0017 wt %) in the crust of Earth and can be extracted with a much reduced cost. [9, 10] In addition, the current collector (Cu) in LIBs can be replaced by aluminum as no formation of K-Al alloys at low potential, thus decreasing the production cost of battery. All of these intrinsic advantages of KIBs enable them to be promising candidates in energy storage field; however, the exploration of KIBs electrode materials is full of challenge due to the larger radius size of K^+ (1.38 Å) and its highly reactivity. [7]

Recently, the research attention on KIBs' electrode materials is mainly focused on carbonaceous materials, alloying-type materials, transition metal oxides and dichalcogenides (TMDs) (TiS_2 or MoS_2). [11-17] However, it has to be noted that the electrochemical performances for potassium storage of the aforementioned materials are much inferior to their corresponding lithium counterparts. Specifically, the in-depth understanding the related

reaction mechanisms for potassium storage still remains a great challenge. Among various 2D TMDs, TiSe_2 has been widely investigated on its charge density wave (CDW) instability owing to its quasi-two-dimensional electronic structures. [18] In the meantime, its application potential in rechargeable batteries gains much emphasis considering TiSe_2 features large interlayer space and much higher electrical conductivity. [19] The electrochemical behaviours of TiSe_2 in Mg-ion battery and Na-ion battery have been investigated, and both cases could exhibit promising reversibility and decent cycling performances. [20, 21] To date, there has been no report regarding the electrochemical behaviour of TiSe_2 for potassium and lithium storage. Considering the larger interlayer space, it can be speculated that TiSe_2 might be a promising alternative electrode material for KIBs. In this work, we, for the first time, systematically investigated the potassium/lithium storage behaviours of TiSe_2 with specific emphasis on intercalation reaction kinetics and the related mechanisms. The intercalation reaction kinetics was studied by means of GITT analysis and the intercalation reaction mechanisms of TiSe_2 were uncovered based on *in-situ* XRD, *ex-situ* TEM, and *ex-situ* XPS characterizations.

2. Experimental Section

2.1 Material synthesis and characterization

TiSe_2 was synthesized by a powder sintering method at high temperature (650 °C). Typically, stoichiometric amount Ti and Se powder was mixed uniformly and sealed in an evacuated quartz tube. Subsequently, the quartz tube was placed in Muffle furnace and calcined at 650 °C for 8 h (5 °C min⁻¹) to obtain the target product. X-ray diffraction (XRD) data was collected by a GBCMMA diffractometer with Cu K α radiation at a scanning rate of 1° min⁻¹. The X-ray photoelectron spectroscopy (XPS) spectrum was tested on a Phoibos X-ray photoelectron spectrometer (100 Analyser, SPECS, Germany, AlK α X-rays). The morphologies of TiSe_2 were captured by field-emission scanning electron microscopy

(FESEM) (JEOL 7500) and transmission electron microscope (TEM) (JEOL 2010). Raman measurement was performed with a Raman JY HR800 Spectrometer.

2.2 *Electrochemical measurements*

Electrochemical performance was obtained by testing CR 2032 coin cells, which were assembled in an argon-filled glove box. The working electrodes were fabricated by mixing 70 wt.% active materials (as-prepared TiSe_2), 20 wt.% Super P and 10 wt.% poly(vinyl difluoride) (PVDF) in N-methyl-2-pyrrolidone (NMP) solvent. Then the slurry was uniformly coated onto Al foil, vacuum dried at 80 °C for overnight, pressed at 200 Kg cm⁻², and punched into discs. In terms of batteries assembling, Li foil was used as the counter electrode in LIBs, K metal was used as the counter electrode in KIBs, and glass fibre paper was used as the separators. For K-ion batteries testing, the electrolyte was 0.8 M KPF_6 dissolved in EC/DEC (1:1 in volume). In terms of Li-ion batteries testing, the electrolyte was 1 M LiPF_6 solution in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1 in volume). Cyclic voltammetry (CV) was performed by a Biologic VMP-3 electrochemical work station over the potential range of 1.0-3.0 V and 1.5-3.0 V for K- and Li-ion batteries, respectively, at a scanning rate of 0.1 mV s⁻¹. Galvanostatic discharge/charge measurements and Galvanostatic Intermittent Titration Technique (GITT) tests were carried out using a LAND Battery Tester at a voltage window of 1.0-3.0 V and 1.5-3.0 V for K- and Li-ion batteries, respectively. In the measurement, the cell was repeatedly discharged/charged at 20 mA g⁻¹ (~0.15 C) for 10 min (τ), followed by a potential relaxation step for 50 min at open circuit. Thus the cell was in a steady-state and the voltage was maintained at a stable value (E_s). All electrochemical studies were carried out at room temperature.

2.3 *In-situ XRD measurement*

The *in-situ* XRD data was collected with Bruker D8 Focus X-ray diffraction instrument. In terms of *in-situ* XRD observation, TiSe₂ was mixed with carbon black with a mass ratio of 4:1, and then ground uniformly by hand in agate mortar to form the powder electrode. In a live and specially designed *in-situ* cell, metallic Be disc was used as X-ray transmission window thus the powder electrode, separator, metal discs as well as electrolyte were added in sequence to assemble the battery. The detailed structure of *in-situ* battery was described in related paper. [22] In terms of *in-situ* batteries testing, the TiSe₂ powder electrode was coupled with potassium/lithium discs and operated at a small current density within a voltage window of 1.0-3.0 V and 1.5-3.0 V, respectively. The obtained *in-situ* XRD patterns and voltage profiles are discussed in the following section.

3. Results and Discussion

The morphology of the as-prepared TiSe₂ and its phase characterizations are illustrated in **Figure 1**. According to the Rietveld refined XRD pattern of TiSe₂ as shown in **Figure 1a**, the observed Bragg positions are indexed to a hexagonal lattice with *P-3m1* (No. 164) space group and lattice parameters of **a =b=** 3.54048 Å and **c =** 6.00793 Å (Table S1, Supporting Information). Through the [110] direction, the crystal structure of TiSe₂, together with the octahedral and tetrahedral sites is presented in **Figure 1b**. The Ti atom bonds with its adjacent six Se atoms, which forms Ti-Se octahedron unit cell and constitutes the basic framework of TiSe₂. The interlayer space (0.601 nm) between two layers provides ideal accommodation sites for alkaline metal ions and the intercalation sites are displayed according to previous reports.[23-25] Therefore, the K⁺ or Li⁺ are intercalated/deintercalated into the specified sites thus offer reversible capacities during the discharge/charge processes. The detailed intercalation mechanisms of K⁺/Li⁺ are discussed in the following sections. From the SEM image in Figure S1 (Supporting Information), the TiSe₂ exhibits stacked layers and typical plate-like structure. In addition, **Figure 1c** gives the TEM morphology of nanosheet TiSe₂ and its crystal lattice fringes in HRTEM (**Figure 1d**) reveal the lattice spacing of 0.27 nm, which

is in good agreement with the (101) plane of TiSe_2 . Moreover, two vibration peaks of Raman spectra (**Figure 1e**), which centered at around 199.5 and 134.7 cm^{-1} respectively, correspond to A_{1g} and E_g symmetries of TiSe_2 . [26]

The electrochemical properties of TiSe_2/K and TiSe_2/Li cells were first investigated at a current density of 65 mA g^{-1} (0.5 C). As described in **Figure 2a**, for potassium storage, the discharge/charge curves have four voltage plateaus at around 2.05/2.31, 1.76/2.17, 1.27/1.88, and 1.19/1.43 V, respectively. And the cell delivers the initial charge capacity of 92.7 mA h g^{-1} , indicative of the uptake of $\sim 0.71 \text{ K}^+$ every TiSe_2 formula (**Figure 2a** and Figure S2a, Supporting Information), as well as maintains the reversible capacity to be 64.7 mA h g^{-1} during the 100th cycle. **Figure 2b** shows the CV curves of TiSe_2/K within the potential range of 1.0-3.0 V at a scan rate of 0.1 mV s^{-1} . There are four reversible redox couples located at 1.97/2.32, 1.75/2.16, 1.27/1.86, and 1.17/1.43 V, which is consistent with the profiles of the discharge/charge curves. While in **Figure 2c**, the first charge capacity of TiSe_2/Li reaches 121.6 mA h g^{-1} , corresponding to the deintercalation of $\sim 0.93 \text{ Li}^+$ per TiSe_2 structure unit, and the reversible capacity decreases to 109.7 mA h g^{-1} during the 100th cycle (Figure S2b, Supporting Information). As can be seen from the first three CV curves of TiSe_2/Li (**Figure 2d**), three redox peaks at around 1.92/2.20, 1.71/2.05, and 1.63/1.83 V are in good agreement with the discharge/charge curves. The rate capabilities and long cycling performances of TiSe_2/K and TiSe_2/Li are shown in **Figure 2e-2g**. The average charge capacities of TiSe_2/K are 89.0, 75.0, 66.6, 58.1, 52.3, 47.9, and 44.5 mA h g^{-1} at the current densities of 50, 100, 200, 400, 600, 800, and 1000 mA g^{-1} , respectively. When the current density recovers to 50 mA g^{-1} , the charge capacity increases to 78.5 mA h g^{-1} . By contrast, TiSe_2 exhibits better rate capability for lithium storage, and the charge capacity still has a high capacity retention of 90.8 mA h g^{-1} at 1000 mA g^{-1} . The charge capacity recovers to 117.3 mA h g^{-1} after switching the current density to 50 mA g^{-1} . It is worth mentioning that the capacity of TiSe_2/K degrades more quickly as compared to TiSe_2/Li . TiSe_2/K and TiSe_2/Li maintain capacity retention of

61.1% and 80.7%, respectively, after 300 cycles even at a current density of 400 mA g⁻¹. Particularly, the K⁺/Li⁺ intercalation capacity of TiSe₂ is close to that of TiS₂ though the theoretical capacity of TiSe₂ (130.2 mA h g⁻¹) is much lower than TiS₂ (240.0 mA h g⁻¹).^[15, 16] The result suggests that faster intercalation reaction kinetics is achieved in TiSe₂ as compared to TiS₂.

In order to gain a better understanding of the reaction kinetics of TiSe₂/K and TiSe₂/Li, GITT is used to evaluate the chemical diffusion coefficients of K⁺ and Li⁺. **Figure 3a** presents the GITT profiles of TiSe₂/K during the 1st cycle. One typical single step of titration at around 1.73 V is presented in **Figure 3b** with related parameters schematically labelled. The D_{K+} can be determined by applying Fick's second law of diffusion and was calculated by Eq. (1) ^[27, 28]:

$$D_{K^+} = \frac{4}{\pi} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\tau (dE_\tau / d\sqrt{\tau})} \right)^2 \quad (\tau \ll L^2 / D_{K^+}) \quad (1)$$

Here, the m_B, V_M, and M_B are the mass, the molar volume, and the molecular weight of the electrode material. A is the surface area of the electrode, and L is the diffusion length. In view of the linear relationship between cell voltage and τ^{1/2} (Figure S3, Supporting Information), thus the Eq. (1) can be further simplified as Eq. (2):

$$D_{K^+} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \quad (2)$$

Based on the calculated results, the profiles of log (D_{K+}) vs. voltage are displayed in **Figure 3c** and the D_{K+} values are ranging from 3.37×10⁻¹² to 1.99×10⁻⁹ cm² s⁻¹ during the whole discharge/charge processes. The GITT profile of TiSe₂/Li during the 1st cycle together with its one single titration step at around 1.93 V is illustrated in **Figure 3d-3e**. The chemical coefficients of lithium (D_{Li+}) are between 2.54×10⁻¹¹ to 6.73×10⁻¹⁰ cm² s⁻¹ in the whole voltage window (**Figure 3f**). The characteristics of the chemical coefficients can be classified

into two regions: ions intercalation/deintercalation processes and non-intercalation/deintercalation stages, which can be also observed in many typical intercalation-type electrode materials. [28-30] Initially (from open circuit voltage to where the first voltage plateau appears), the values of D_{K^+} are in the range of 3.58×10^{-11} to $8.92 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, which is around one order of magnitude lower than that of D_{Li^+} (between 2.73×10^{-10} and $4.67 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) in TiSe_2/Li system. As the intercalation reaction happens, both the diffusion coefficients of K^+ and Li^+ decrease with the formation of new phases. Specifically, the values of D_{K^+} at the first K^+ -intercalation stage vary from 6.54×10^{-12} to $3.37 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, accompanied with the phase change from TiSe_2 to $\text{K}_{0.25}\text{TiSe}_2$. At the same time, the diffusion coefficients of Li^+ range from 3.53×10^{-10} to $1.13 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ when the phase evolves from TiSe_2 to $\text{Li}_{0.33}\text{TiSe}_2$, which is around two orders of magnitude higher than that of K^+ . In the next stage, the phase $\text{K}_{0.25}\text{TiSe}_2$ continually transforms into $\text{K}_{0.58}\text{TiSe}_2$ with further K^+ intercalation, and the diffusion coefficients of K^+ in this phase transformation region are in the range of 8.94×10^{-10} - $5.92 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. Interestingly, the values of D_{Li^+} in this phase transformation stage are in the range of 3.50×10^{-10} - $4.28 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, which is slightly lower than D_{K^+} . This might correlate with the structural difference between $\text{K}_{0.25}\text{TiSe}_2$ and $\text{Li}_{0.33}\text{TiSe}_2$ during further intercalation. The much larger layer distance of $\text{K}_{0.25}\text{TiSe}_2$ ($c=42.355 \text{ \AA}$) might make it a bit easier for K^+ intercalation than Li^+ from $\text{Li}_{0.33}\text{TiSe}_2$ ($c=25.983 \text{ \AA}$) to LiTiSe_2 . The schematic illustrations of the crystal structures of these intermediate phases are presented in Figure S8-S9 (Supporting Information). Finally, the diffusion coefficients of K^+ decrease to 5.00×10^{-11} - $1.79 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ along with the phase transformation from $\text{K}_{0.58}\text{TiSe}_2$ to K_xTiSe_2 . In addition, the values of D_{Li^+} change slightly (3.91×10^{-10} - $9.10 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) with the formation of LiTiSe_2 , which is approximately one order of magnitude higher than that of D_{K^+} . While in the reverse charge process, nearly identical evolution of diffusion coefficients of K^+ and Li^+ can be observed as compared to discharge process. The value of D_{K^+} is determined to be 4.16×10^{-10} , 1.54×10^{-10} , and 8.94×10^{-12}

$\text{cm}^2 \text{ s}^{-1}$ along with the phase change from K_xTiSe_2 to $\text{K}_{0.58}\text{TiSe}_2$, $\text{K}_{0.58}\text{TiSe}_2$ to $\text{K}_{0.25}\text{TiSe}_2$, and $\text{K}_{0.25}\text{TiSe}_2$ to TiSe_2 , respectively. Meanwhile, D_{Li^+} is 5.47×10^{-10} and 2.54×10^{-11} accompanied with the phase evolution from LiTiSe_2 to $\text{Li}_{0.33}\text{TiSe}_2$, and $\text{Li}_{0.33}\text{TiSe}_2$ to TiSe_2 , which is one order of magnitude higher than that of D_{K^+} . On the basis of the aforementioned discussion, it can be concluded that Li^+ exhibit faster diffusion kinetics in TiSe_2/Li system than K^+ in TiSe_2/K system, which is the intrinsic reason for the better rate capability of TiSe_2/Li as depicted in the **Figure 2e** and **2f**.

The intercalation reaction mechanisms of TiSe_2/K and TiSe_2/Li were systematically investigated by means of *in-situ* XRD, *ex-situ* TEM, and *ex-situ* XPS. **Figure 4a** shows the *in-situ* XRD patterns of TiSe_2/K during the first two cycles, and the voltage profiles are presented in **Figure 4d**. Worth noting, the peaks at 38.7° and 41.4° are ascribed to BeO , which are arising from the X-ray transmission window (Be). At the beginning, the TiSe_2/K cell presents an initial open circuit voltage of 2.90 V and the diffraction peaks displayed in **Figure 4a-4c** and Figure S4a (Supporting Information) are originating from the pristine TiSe_2 phase. In the first stage ($0 < x < 0.25$), the relative intensity of (001), (002), (101), and (102) diffraction peaks becomes gradually weakened with Bragg positions unchanged. Upon further intercalation, three newly formed peaks can be indexed to (006), (106), and (108) planes of $\text{K}_{0.25}\text{TiSe}_2$ (PDF No. 32-0862) (Figure S4b, Supporting Information), as indicated by the black dash circles in **Figure 4a-4b**. Subsequently, the biphas (TiSe_2 and $\text{K}_{0.25}\text{TiSe}_2$) undergoes a gradual transformation to triphase accompanied with the formation of $\text{K}_{0.58}\text{TiSe}_2$ (PDF No. 32-0863) (Figure S4c, Supporting Information). As the voltage falls to 1.0 V, the intercalation reaction ends with one newly formed phase, K_xTiSe_2 ($0.58 < x < 1$), with two characteristic diffraction peaks marked by pink dash circles. During the charge process, the K_xTiSe_2 ($0.58 < x < 1$) phase transforms into $\text{K}_{0.58}\text{TiSe}_2$, $\text{K}_{0.25}\text{TiSe}_2$, and TiSe_2 in sequence along with K^+ deintercalation. The existence of an unknown phase K_yTiSe_2 in the fully charged state implies the partially irreversible structural evolution. A slightly different phase transformation

behaviour was reported in the TiS_2/K system.[15, 16] As illustrated by Tian *et al.*, the discharged phase $\text{K}_{0.88}\text{TiS}_2$ cannot recover back to TiS_2 during the initial cycle due to the structural distortion induced by K^+ intercalation.[15] Li *et al.*, suggested that K^+ intercalation favours a Daumas-Hérol model accompanied by the partially irreversible phase change from TiS_2 to $\text{K}_{0.56}\text{TiS}_2$. [16] In contrast, for Li^+ intercalation/deintercalation, TiSe_2 presents continuous and periodical phase evolution from TiSe_2 to $\text{Li}_{0.33}\text{TiSe}_2$ and then to LiTiSe_2 (**Figure 4g-4i** and Figure S5a, Supporting Information). Notably, the Li^+ deintercalation ends with the re-formation of TiSe_2 phase and no observable unknown phases can be found in **Figure 4g-4i**, suggesting the excellent reversibility of Li^+ intercalation, which is similar to the Li^+ intercalation/deintercalation reaction in TiS_2 . [31, 32] On the other hand, TiSe_2 phase can still be observed after the first K^+ intercalation reaction, indicating the incomplete potassiation reaction of TiSe_2 due to the sluggish reaction kinetics, whereas no TiSe_2 phase can be detected for lithium counterpart.

The crystal structure of TiSe_2 is illustrated in **Figure 4e-4f** in order to visually elucidate the structural evolutions. As depicted in **Figure 4e-4f**, we chose z -axis along the c -direction to present the $2 \times 2 \times 1$ cell structure of TiSe_2 with the octahedral sites (Oh) and the tetrahedral sites (Tr) were schematically labelled. Among the $2 \times 2 \times 1$ cell structure, each Oh site is surrounded by its adjacent four Tr sites and every single TiSe_2 unit has one Oh site and two Tr sites. [31, 33-35] Furthermore, the much lower energy barrier of Oh sites (-0.55 eV) compared to Tr sites (-0.19 eV) was demonstrated favorable towards intercalation of alkali atoms, which was proved by Ramirez *et al.* through total-energy density functional theory calculations. [35-37] Therefore, the Oh sites at most accommodate one Li^+ or K^+ , and thus TiSe_2 possesses theoretical capacity of $130.25 \text{ mA h g}^{-1}$ based on the redox couple of $\text{Ti}^{4+}/\text{Ti}^{3+}$. Here, we re-examine the value of x in K_xTiSe_2 after discharging to 1.0 V from the perspective of capacity. According to the capacity value ($136.3/92.7 \text{ mA h g}^{-1}$ at 0.5 C) obtained from the discharge/charge curves shown in **Figure 2a**, the intercalated/deintercalated K^+ are

determined to be $\sim 1.05/0.71$. And, the specific capacity originated from the GITT profile indicates the intercalated/deintercalated K^+ is $\sim 1.18/0.74$. Considering $TiSe_2$ is not fully involved in the intercalation reaction due to the sluggish reaction kinetics, there is considerable capacity contributed by the electrolyte-involved side reactions. From the above analysis, the number of intercalated K^+ at the fully discharged state (1.0 V) should be around 0.7, corresponding to the formation of $K_{0.7}TiSe_2$. Hence, the phase evolution from $TiSe_2$ to K_xTiSe_2 during discharge process can be written as Eq. (3):

And the charge process proceeds following Eq. (4):

With regard to $TiSe_2/Li$, it is no doubt that $TiSe_2$ experiences a reversible intercalation reaction with one Li^+ intercalated into $TiSe_2$ host according to the results presented in **Figure 4g-4i** and Figure S5 (Supporting Information). And the phase evolution during Li^+ intercalation reaction can be illustrated by Eq. (5):

The chemical compositions of the intermediate phases during K^+/Li^+ intercalation reaction were determined by *ex-situ* X-ray photoelectron spectroscopy (XPS), as shown in Figure S11-S12 (Supporting Information). In the discharged state as shown in Figure S11a (Supporting Information), the typical peaks located at ~ 457 and ~ 462.5 eV can be assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$ electronic configurations, respectively. [38, 39] In addition, the 2p core level peaks of Ti are broadened into four characteristic peaks, which is a result of the formation of two types of Ti atoms. Among which, the peaks positioned at ~ 458.5 and ~ 464.3 eV are characteristic peaks of Ti^{4+} , which can be ascribed to the residual $TiSe_2$. The peaks at ~ 457.5 and ~ 462.5 eV can be attributed to Ti^{3+} of K_xTiSe_2 , which are arising from the

reduction of Ti^{4+} after K^+ intercalation. When charged to 3.0 V, the relative intensity of the characteristic peaks of Ti^{3+} is largely reduced, whereas the intensity of Ti^{4+} peaks increases significantly, confirming the depotassiation reaction. Besides, characteristic peaks of K 2p_{3/2} at ~292.9 eV as well as K 2p_{1/2} at ~295.7 eV are observed in the discharged state, indicating the existence of K^+ in K_xTiSe_2 .^[40] By contrast, in the charged state, the K 2p_{1/2} peak at ~295.7 eV totally disappears and the peak intensity of K 2p_{3/2} at ~292.9 eV decreases accordingly, revealing the de-composition of K_xTiSe_2 . With regard to the lithium counterpart, the transformation of Ti^{3+} and Ti^{4+} (Figure S12, Supporting Information) shows similar behaviour during Li^+ intercalation/deintercalation reaction. The results evidently prove the formation of LiTiSe_2 after Li^+ intercalation as well as the transformation from LiTiSe_2 to TiSe_2 during Li^+ deintercalation process.

In order to gain further in-depth understanding of the structural evolutions during K^+/Li^+ intercalation/deintercalation processes, *ex-situ* HRTEM were conducted at the discharged/charged states. Meanwhile, the TEM images at the corresponding states where the HRTEM images were captured are presented in Figure S13 (Supporting Information). **Figure 5a** displays the HRTEM image at the fully discharged state, and expanded as well as distorted lattice fringes can be observed. The lattice spacing of 0.80 nm, can be assigned to the (003) planes of $\text{K}_{0.58}\text{TiSe}_2$ (PDF NO.32-0863), which can be confirmed by the (003) diffraction spots in the corresponding FFT image (**Figure 5b**). Clearly, the obvious structural distortions caused by intercalation of K^+ can also be seen in the studies of potassiation of TiS_2 .^[15, 16] At the fully charged state, the lattice spacings of 0.29 and 0.31 nm correspond well with the (002) and (100) facets of TiSe_2 , respectively (**Figure 5a**). In the meantime, a set of sharp spots ((002), (100), and (101)) along the zone axis of [1-21] in the FFT (**Figure 5d**) image further demonstrate the re-formation of TiSe_2 after the deintercalation of K^+ . **Figure 5e** shows the HRTEM image of TiSe_2 at the fully Li^+ intercalation stage. In contrast to the K^+ intercalation depicted in **Figure 5a**, the expanded lattice spacings of 0.32 and 0.28 nm can be ascribed to

the (002) and (011) planes of LiTiSe₂. Particularly, the FFT image in **Figure 5f** clearly reveals the good crystallinity of the generated LiTiSe₂ with the diffraction spots of (002), (011), and (012) along the zone axis of [2-1-1]. After fully charged to 3.0 V, the lattice fringe shown in **Figure 5g** can be index to the (002) plane of TiSe₂ with a *d*-spacing of 0.29 nm. The (100) and (002) diffraction spots along the zone axis of [-12-1] further confirm the presence of TiSe₂. On the basis of the aforementioned analysis, it can be concluded that TiSe₂ undergoes a completely reversible Li⁺ intercalation/deintercalation reaction with the reversible formation of Li_{0.33}TiSe₂ and LiTiSe₂; whereas the K⁺ intercalation/deintercalation process is partially reversible accompanied with the formation of K_{0.25}TiSe₂, K_{0.58}TiSe₂, and K_{*x*}TiSe₂ (*x*≈0.7).

4. Conclusion

In summary, the electrochemical K⁺ and Li⁺ intercalation behaviours in TiSe₂ were for the first time reported. The diffusion kinetics of K⁺ and Li⁺ in TiSe₂ were systematically studied by means of GITT. The calculated diffusion coefficients of K⁺ are ~1-2 orders lower than Li⁺ counterpart. On the other hand, the mechanisms for the electrochemical intercalation reactions were also investigated by *in-situ* XRD, *ex-situ* XPS, as well as *ex-situ* TEM. TiSe₂ experiences three phases' stages with partially reversible formation of K_{0.25}TiSe₂, K_{0.58}TiSe₂, and K_{*x*}TiSe₂ (*x*≈0.7) during K⁺ intercalation/deintercalation. Meanwhile, the Li⁺ intercalation/deintercalation proceeds via completely reversible formation of phases Li_{0.33}TiSe₂ and LiTiSe₂. The results would provide new insights into developing intercalation reaction-based electrode materials for rechargeable alkali batteries.

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Conflict of interest

The authors declare no competing financial interest.

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Figure Captions

Figure 1. (a) XRD Rietveld refinement pattern of TiSe_2 ; (b) crystal structure of TiSe_2 with octahedral sites (Oh) as well as the adjacent tetrahedral sites (Tr); (c) TEM and (d) HRTEM images of TiSe_2 ; (e) Raman spectra of TiSe_2 .

Figure 2. (a) The galvanostatic discharge/charge curves of TiSe_2 in K-ion battery at 65 mA g^{-1} (0.5 C) between 1.0 and 3.0 V; (b) the first three CV curves of TiSe_2 in K-ion battery. (c) The galvanostatic discharge/charge curves of TiSe_2 in Li-ion battery at 65 mA g^{-1} (0.5 C) between 1.5 and 3.0 V; (d) the first three CV curves of TiSe_2 in Li-ion battery. Rate capabilities of TiSe_2 in (e) K-ion battery and (f) Li-ion battery. (g) Cycling performances of TiSe_2 in K-ion and Li-ion batteries at 0.4 A g^{-1} .

Figure 3. GITT curves of TiSe_2 in K-ion (a) and Li-ion battery (d) as a function of time in the voltage range of 1.0-3.0 V and 1.5-3.0 V during discharge/charge processes; (b) Scheme for a single step of a GITT experiment for K-ion (b) and Li-ion battery (e) during the first discharge process: τ (constant current pulse time), $\Delta E\tau$ (total change of cell voltage during constant current pulse neglecting the IR-drop) and ΔE_s (change of the steady-state voltage). D_{K^+} (c) and D_{Li^+} (f) values in the TiSe_2/K and TiSe_2/Li cells during the first discharge/charge process.

Figure 4. Structural evolutions of a TiSe_2/K cell during in-situ XRD discharge/charge processes. The peaks' evolution in the 2θ range from 10.0 to 15.0° (a); from 28.0 to 35.0° (b); from 38.0 to 43.0° (c). (d) The corresponding discharge/charge curves of the in-situ TiSe_2/K cell. (e) Cell structure of TiSe_2 along $[001]$ direction before K^+/Li^+ intercalation process; (f) structure of TiSe_2 at the end of intercalation step. Structural evolutions of a TiSe_2/Li cell during in-situ XRD discharge/charge processes. The peaks' evolution in the 2θ range from 11.0 to 16.0° (g); from 27.0 to 34.0° (h); from 38.0 to 43.0° (i). (j) The corresponding discharge/charge curves of the in-situ TiSe_2/Li cell.

Figure 5. The ex-situ HRTEM images and corresponding SAED patterns of the TiSe_2/K cell at a discharged state of (a-b) 1.0 V and charged state (c-d) of 3.0 V. The ex-situ HRTEM images and corresponding SAED patterns of the TiSe_2/Li cell at a discharged state of (e-f) 1.5 V and charged state (g-h) of 3.0 V.

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