Synthesis of nickel doped anatase titanate as high performance anode materials for lithium ion batteries

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Abstract: Novel Ni-doped titanate **derived from protonated layered titanate** has been fabricated *via* a simple ion-exchange process at room temperature. **The as-synthesized product was calcined at 400 °C for 3h to obtain the Ni-TiO₂ (anatase).** The crystal structure of Ni-TiO₂ was studied by X-ray diffraction (XRD) and the surface chemistry was studied by X-ray photoelectron spectroscopy (XPS). It was found that doped nickel ions had inhibition effects on the crystallization of TiO₂ during calcination. The electrochemical properties of **Ni-TiO₂ and undoped TiO₂** were both tested as anode materials for lithium-ion batteries at room temperature. While the undoped sample exhibited a mediocre performance, having a discharge capacity of 132 mAhg⁻¹ after 50 cycles, the nickel-ion doped sample demonstrated noticeable improvement in both of its discharge capacity and rate capability; with a high capacity value of 226 mAhg⁻¹ after 50 cycles. This improvement of lithium ion storage capability of Ni-TiO₂ can be ascribed to the Ni-doping effect on crystallinity and the modification of electrode/electrolyte interface of the **TiO₂ structure**.

Keywords: **protonated layered titanate**; ion-exchange; lithium-ion batteries

1. Introduction

For several decades, there has been a steady increase in the demand for high performance and long-lasting rechargeable batteries for a wide range of applications, from portable electronics to hybrid vehicles [1-4]. As one of the most widely used energy storage devices, Li-ion batteries (LIBs) have high intrinsic energy density and thus are promising candidates for these applications [5, 6]. However, current LIB technologies are still unable to meet the soaring industrial demand that requires a significant increase of power supply capacity. After a careful analysis of the major components of LIBs and recent studies, it is not difficult to conclude that although electrolyte plays an important role in the performance of LIBs, our choices are indeed limited to electrodes for a remarkable increase of the discharge capacity. As the most critical part of batteries, the performance of electrodes (including both anodes and cathodes) depends directly on their chemical compositions, crystal structure, microstructural, etc.; it is reasonable to say that one of the top priorities for the improvement on LIB performance is the exploration of highly functional electrode materials. After decades of research, quite a few electrode materials have been selected for further investigation. Among them is titania (TiO_2) as the anode for LIBs. Titania is a promising anode material because of its high chemical stability, non-toxicity, abundance, and low cost [7-10]. Among different TiO_2 polymorphs, anatase TiO_2 is considered as the one of most promising candidates for energy storage due to its easy fabrication, fast Li^+ insertion–extraction reactions, and high theoretical insertion capacity [11-14]. However, in most applications the real capacity of anatase

TiO₂ is lower than the predicted maximum of 335 mAhg⁻¹ [10, 15] due to the phase transition from tetragonal crystal structure to orthorhombic crystal structure and the resulting 1-D diffusion limitation in the Li-ordered Li_{0.5}TiO₂ [16]. To solve this problem, it is essential to circumvent the impediment of pure Li_{0.5}TiO₂. Fabricating a novel TiO₂-based compound by modifying the anatase TiO₂ chemical composition provides a feasible way to overcome this limitation. Doping is most widely employed in attempts of fabricating TiO₂-based new compound and its effectiveness has been demonstrated. For instance, there are several papers reporting the fabrication of nickel ion doped TiO₂, using the methods of hydrothermal [17, 18], sol-gel [19] and hot solution reaction [20], respectively. However, routine doping processes are mostly complicated and time-consuming. Besides doping, some other efforts have also been made to modify the surface chemistry of TiO₂ by coating, such as atomic layer deposition [21] and solution-based coating [22]. These methods have been successful in small systems but the scale-up either poses an energy input/output efficiency question or involves technical challenges, especially the challenges associated with homogenous coverage [23]. Therefore, a bulk synthesis and simple uniform doping process is still necessary for further exploration and application of anatase TiO₂.

Herein, we adopt a two-step strategy for synthesis of surface-doped TiO₂. First, layered protonated titanate structures were synthesized *via* an aqueous solution based reaction at room temperature. Then, the prepared layered structure was easily doped by nickel ions through an ion-exchange process at room temperature. This Ni-TiO₂ sample turned into anatase structure after calcination and exhibited noticeable

performance improvement in electrochemical tests when used as anode materials, which indicated the prospects of surface doped TiO₂ for applications in LIBs.

2. Experimental

2.1 Preparation of Ni-doped TiO₂ structure.

For the synthesis of Ni-doped TiO₂ structure, the precursor of layered protonated dititanate was first prepared *via* an aqueous solution based reaction at room temperature similar to reported in the literature [24]. In a typical synthesis process, 2.9762 mL of titanium (IV) isopropoxide (TIP, 97%, Sigma-Aldrich) was added to 10 mL of anhydrous ethanol (>99.5%, Anhydrous, Sigma-Aldrich), followed by the addition of 40 mL of ammonium hydroxide (ACS, 30%, Alfa Aesar) under stirring. The milky white suspension was kept static for 10 min and then centrifuged; the precipitate was washed with DI water three times and suspended in 25 mL of ammonium carbonate (ACS, Fisher Chemical) solution (1.5 M). Then, 3 mL of hydrogen peroxide (ACS, 30.0 to 32.0 %, Fisher Chemical) was added to the solution and stirred overnight. The obtained products were washed with DI water three times and dried in air at 50 °C. After this treatment, the obtained precursors were dispersed in 200 mL of nickel chloride (98%, Anhydrous, Alfa Aesar) solution (0.09 M) under constant stirring for 2 h. After that, the powders were washed three times by DI water to remove excess ions and dried in air at 50 °C. For comparison, the precursor powders were also doped with Mn ions in the same concentration of manganese nitrate tetrahydrate (98%, Alfa Aesar) solution. Finally, the doped and undoped TiO₂ powders were calcined at 400 °C for 3 h. Within this study, the samples are designated

as TiO₂-P (precursor), TiO₂-400 (after calcination without ion doping), TiO₂-Ni-400 (after the Ni ion-exchange process and calcination), TiO₂-Mn-400 (after the Mn ion-exchange process and calcination).

2.2 Structural characterization.

The morphology of the obtained samples were studied with scanning electron microscopy (SEM, FEI Quanta 200) and Transmission electron microscopy (TEM, JEM-2100F) with accelerating voltage at 20 kV and 200kV respectively. The crystal structures were determined by X-ray diffraction (XRD, Bruker D2) on a Scintag diffractometer with CuK α_1 radiation ($\lambda = 1.54060 \text{ \AA}$) at a scanning rate of $0.017^\circ \text{ s}^{-1}$ in the 2θ range from 5° to 75° . The surface element composition was measured by energy dispersive spectroscopy (EDS) using the FEI Quanta 200 and X-ray photoelectron spectroscopy (PHI Quantera) with Al K α X-rays (monochromatic, beam size=100 μm). With respect to XPS analyses, survey scans were used to qualitatively identify elemental composition and were collected using the following parameters; 100 μm spot size, 25 W, 15 kV, 280 eV pass energy, 1 eV step size, and a binding energy range of 0-1100 eV. To determine chemical states and relative compositions of the different components, high resolution scans were then acquired using identical spot size, power, and voltage as the survey scans, however the pass energy and step size was reduced to 26 eV and 0.025 eV, respectively. The nitrogen adsorption and desorption isotherms were collected at 77 K in the range of relative pressures of 0.0002-0.99P/P₀ using a TriStar II 3020 surface area and porosity measurement system (Micromeritics Instrument Corp.) and used for estimation of the

pore size distribution in the 1.7-300 nm range.

2.3 Electrochemical evaluation.

Electrochemical impedance spectroscopy (EIS) studies were carried out using a Bio-Logic VMP3 Potentiostat analyzer. The applied AC perturbation was 5 mV and the frequency range was from 100 kHz to 0.1 Hz. Lithium ion battery performance tests were carried out with a half-cell configuration using CR-2032 coin cells. Li foil was used as both the counter and reference electrode. The working electrode was prepared by mixing active materials (80%), black carbon (Alfa Aesar, 10%), and polyvinylidene fluoride (PVDF, Alfa Aesar, 10%) in N-methyl-2-pyrrolidone (NMP, Alfa Aesar). After uniform stirring, the above slurries were coated on copper foils and dried at 120 °C in vacuum for 6 h. Then, the electrode was pressed and cut into disks before assembly in an Argon-filled glove box for coin-cell assembling. 1 M LiPF₆ in a mixed solution of ethylene carbonate and diethyl carbonate (1:2 volume ratio, Novolyte, USA) was used as the electrolyte. Galvanostatical discharge/charge tests were performed using an Arbin-BT 2000 measurement system in the potential window of 1-2.5 V versus Li⁺/Li at different current densities of 30 mA g⁻¹, 150 mA g⁻¹ and 500 mA g⁻¹ at room temperature.

3. Results and discussion

3.1 Characterization of Ni and Mn-doped TiO₂ structures.

As shown in Fig. 1a, the low-resolution scanning electron microscope (SEM) image shows that the synthesized TiO₂ precursor (TiO₂-P) is granular in nature. Furthermore, the transmission electron microscope (TEM) image in Fig. 1b reveals

that a single particle is formed by layered nanosheets overlapping each other. Fig. 1c shows a SEM image of the TiO_2 after calcination at 400 °C for 3 h (TiO_2 -400). Compared to the sample before calcination, there is little noticeable morphology change. Fig. 1d shows the SEM image of the TiO_2 doped with Ni, and then calcined under the same conditions at 400 °C (TiO_2 -Ni-400). As shown in this image, TiO_2 -Ni-400 has a similar morphology to TiO_2 -400. The Mn ion doped sample TiO_2 -Mn-400 also exhibits a similar morphology to TiO_2 -400 and TiO_2 -Ni-400 (Fig. S1). All these images indicate that this ion-exchange process has negligible influence on the morphology of prepared samples. However, obvious differences in crystallinity, surface composition, and surface area can be identified among them through the study of XRD patterns, XPS spectra, and nitrogen adsorption isotherms.

The effect of doped ions on crystallinity evolution of TiO_2 is studied by XRD and the patterns are shown in Fig. 2. In Fig. 2a, the XRD pattern of prepared protonated titanate has two diffraction peaks of $2\theta \approx 9.7^\circ$, 27.6° corresponding to the first and second strongest diffraction peaks of $\text{H}_4\text{Ti}_2\text{O}_6$ (PDF, 047-0124, $a=1.926$, $b=0.378$, $c=0.300$). After calcination at 400 °C for 3 h, the undoped sample TiO_2 -400 shows a typical anatase crystal structure (Fig. 2b). The Ni-doped sample TiO_2 -Ni-400 shows a similar anatase crystal structure but lower peak intensity, which suggests that nickel ions have inhibition effects on the TiO_2 phase transition. This inhibition effect is more noticeable in the case of manganese ion doping. As shown in the same figure, the Mn-doped sample TiO_2 -Mn-400 shows very weak crystalline peaks in its XRD pattern. This inhibition effect was already observed in our previous work [25]. And

some other groups also reported a similar result using a traditional calcination doping process [22, 26]. Besides the crystallinity inhibition effect, it is important to note that diffraction peak shift is identified in TiO₂-400 and TiO₂-Ni-400 patterns. The XRD patterns of these two samples fit the tetragonal structure of anatase well (PDF, 01-071-1166). The lattice parameters a and c for these two samples can be calculated by the software of TOPAS (Bruker, USA). TiO₂-Ni-400 has a larger lattice value of a (3.7938 ± 0.0013 Å) and a smaller value of c (9.4830 ± 0.0027 Å) than that of undoped sample TiO₂-400 ($a = 3.7874 \pm 0.0007$ Å, $c = 9.5021 \pm 0.0016$ Å). The volume of the unit cell for TiO₂-Ni-400 (136.488 Å³) is larger than TiO₂-400 (136.302 Å³). This result suggests that after Ni doping the c axis of the anatase unit cell becomes shorter while the a and b axes become longer, making the tetragonal structure more cubic and the unit cell volume larger. According to previous studies, these two trends are both favorable for reversible lithium ion insertion [16, 27]. In addition, the grain sizes of TiO₂-Ni-400 (33.4 nm) and TiO₂-400 (67.3 nm) are also different based on the calculation from TOPAS, which will affect their specific surface areas after calcination (to be discussed later).

To investigate the doping effect of the ion-exchange process, surface element compositions of TiO₂-400, TiO₂-Ni-400 and TiO₂-Mn-400 were studied by XPS and EDX. As shown in Fig. 3, two distinct peaks at binding energies of 855.5 and 873.8 eV are observed in the Ni 2p high-resolution spectrum of TiO₂-Ni-400 (Fig. 3a), which correspond well to the Ni 2p_{3/2} and Ni 2p_{1/2} peaks of Ni²⁺ [28, 29]. In addition, two small peaks at 861.2 and 879.1 eV can be attributed to 2p_{3/2} sat and 2p_{1/2} sat of

NiO [29, 30]. Fig. 3b shows the Mn 2p high-resolution spectrum of TiO₂-Mn-400. There are two distinct peaks at 641.3 and 653.4 eV, which may be assigned to the 2p_{3/2} and 2p_{1/2} peaks of Mn²⁺. And it can be further confirmed through the unique a broad shake-up satellite peak around 645 eV, which is not shared by the other oxidation states of Mn ions [31, 32]. This suggests that the doped ions' oxidation state do not change after calcination at 400 °C for 3 h. This data provides direct evidence for the presence of Ni and Mn in TiO₂-Ni-400 and TiO₂-Mn-400. Furthermore, the concentration of Ni and Mn ions can also be obtained *via* high resolution scans and the application of empirically derived relative sensitivity factors. The atomic ratio of Ni in TiO₂-Ni-400 is approximately 7 % and the atomic ratio of Mn in TiO₂-Mn-400 is approximately 4 %. Similar results can also be observed in EDS spectra. TiO₂-400 has no nickel or manganese element peak existing in the EDS spectrum (Fig. S2a) while the spectra of TiO₂-Ni-400 and TiO₂-Mn-400 have visible nickel and manganese element peaks respectively (Fig. S2b and 2c).

Ion doping also affects the specific surface area of TiO₂ after calcination. Here, we studied the surface area of different samples by using nitrogen adsorption-desorption measurements. Fig. 4 shows the adsorption and desorption isotherm curves of these three samples. TiO₂-Ni-400 and TiO₂-Mn-400 exhibit adsorption hysteresis that belongs to type IV isotherm curves, indicating that these two samples have mesoporous structures [33]. Their specific surface areas are calculated using the BJH method to be 30.4 m²g⁻¹ and 46.3 m²g⁻¹, respectively. TiO₂-400 shows type II isotherm curves that suggest little porosity. The specific surface area is only 14.5

m^2g^{-1} . Based on the above results, we can deduce that doped ions act as nucleation barriers to inhibit the crystallization and phase transition process during calcination. As a result, the doped TiO_2 has less crystallinity and smaller grains than the undoped TiO_2 . Smaller grain sizes will generally result in smaller particle sizes or the same particle size with larger surface roughness. In other words, a smaller grain size will lead to a larger surface area [34, 35]. As a result, the doped samples have both less crystallinity and larger specific surface areas than the undoped sample after calcination. In addition, this effect varies according to the different ions doped. As shown in Fig. 2b and Fig. 4, the Mn doped TiO_2 ($\text{TiO}_2\text{-Mn-400}$) shows less crystallinity and a larger surface area than the Ni doped one ($\text{TiO}_2\text{-Ni-400}$).

3.2 Electrochemical performance of doped and undoped TiO_2 .

To study the effects of ion doping on the performance of anatase TiO_2 structures as lithium ion storage electrodes, the lithium-ion insertion/extraction properties of anatase ($\text{TiO}_2\text{-400}$) and doped TiO_2 ($\text{TiO}_2\text{-Ni-400}$ and $\text{TiO}_2\text{-Mn-400}$) were evaluated by galvanostatic discharge/charge tests at room temperature for 50 cycles. Fig. 5a-c shows discharge and charge curves of these three samples in the initial and last 3 cycles at a discharge/charge current density of 30 mA g^{-1} in the potential window of 1-2.5 V. It is observed that the initial discharge capacities of $\text{TiO}_2\text{-400}$, $\text{TiO}_2\text{-Ni-400}$ and $\text{TiO}_2\text{-Mn-400}$ are 128 mAh g^{-1} , 448 mAh g^{-1} (this high value was largely due to the parasitic reaction in the first cycle and will not be used for any capacity comparison in the following discussion) and 145 mAh g^{-1} , respectively. As shown in Fig. 5a, $\text{TiO}_2\text{-400}$ shows well-defined plateaus at approximately 1.8 V (discharge process) and

1.9 V (charge process) during the **initial** 3 cycles, which is similar to reported nanostructured anatase [11, 36]. In the last 3 cycles, the lengths of plateaus increased slightly as do the capacities. This result suggests that **the as-synthesized anatase TiO₂ without doping** can only be used as an anode for batteries that do not require high capacity but emphasize good stability. In contrast, Ni doped TiO₂ clearly exhibits higher capacities. As shown in Fig. 5b, TiO₂-Ni-400 exhibits a remarkably higher initial discharge capacity of 448 mAhg⁻¹, which is almost four times that of TiO₂-400. This higher than theoretical value consists of irreversible capacity contributed by side reactions during electrode/electrolyte interface formation, which is demonstrated by subsequent capacity degradation **from 448 mAhg⁻¹ to 271 mAhg⁻¹ in the 2nd cycle.** After this initial capacity degradation, the nickel-doped sample TiO₂-Ni-400 exhibits relatively stable performance during cycling. It is also noticed that discharge and charge plateaus of TiO₂-Ni-400 are much less well defined as compared to those of TiO₂-400. Different from TiO₂-400 and TiO₂-Ni-400, TiO₂-Mn-400 shows a sloping profile of voltage-capacity relationship during discharge and charge processes (Fig. 5c). These curves are typical for electrode materials with low crystallinity, which agrees well with the XRD finding. In addition, although the discharge capacity of TiO₂-Mn-400 in the 1st is a little higher than TiO₂-400, its capacity exhibits noticeable degradation in the subsequent cycles. Fig. 5d displays the cyclic performance of these three samples at different current densities of 30 mA g⁻¹, 150 mA g⁻¹ and 500 mA g⁻¹. As shown in this figure, TiO₂-400 exhibits a good cycling stability. The discharge capacity of TiO₂-400 shows a little increase from 128 mAhg⁻¹ to 132 mAhg⁻¹ after 50

cycles. However, its rate performance is very poor, the discharge capacity is 88 mAhg⁻¹ and 58 mAhg⁻¹ under the current density of 150 mA g⁻¹ and 500 mA g⁻¹, respectively. In contrast, TiO₂-Ni-400 starts with a remarkably high discharge capacity of 448 mAhg⁻¹ followed by a noticeable decay in the 2nd cycle. After this degradation, capacity loss still exists in initial cycles but is much smaller. After 10 cycles, the discharge capacity is 230 mAhg⁻¹, which is more than twice that of TiO₂-400. In addition, the rate capability of TiO₂-Ni-400 is also obviously better than TiO₂-400: its discharge capacity is 200 mAhg⁻¹ at a current density of 150 mA g⁻¹ and 179 mAhg⁻¹ at a current density of 500 mA g⁻¹. When the current density is changed back to 30 mA g⁻¹, its discharge capacity is 221 mAhg⁻¹, which fluctuates slightly in the following cycles and is as high as 226 mAhg⁻¹ after 50 cycles. This value is obviously higher than doped TiO₂ samples reported by other papers. For instance, Djerdj et al. reported a mesoporous Nb-doped TiO₂ synthesized *via* a sol-gel process. The capacity was 168.4 mAhg⁻¹ at a rate of C/8 after 10 cycles [37]. Huang et al. synthesized a conformal N-doped carbon on nanoporous TiO₂ by a solution-phase process. The product exhibited a capacity of 170 mAhg⁻¹ at a current density of 100 mA g⁻¹ and 102 mAhg⁻¹ at a current density of 200 mA g⁻¹ [38]. Fig. 5d also shows that TiO₂-Mn-400 possesses even lower performance than TiO₂-400. It has a lower capacity of 91 mAhg⁻¹ after 50 cycles. And for higher current densities of 150 mA g⁻¹ and 500 mA g⁻¹, the discharge capacity is only 60 mAhg⁻¹ and 36 mAhg⁻¹, respectively. The contrasting performance of TiO₂-Mn-400 and TiO₂-Ni-400 indicates that only certain ion doping can enhance TiO₂'s performance as a lithium ion insertion

electrode. These different ion doping effects on the electrode performance are also in agreement with the result reported by Jiao's group [20].

Above results are also supported by the analysis of the kinetic properties of these samples. Here, **electrochemical** impedance spectroscopy (EIS) was used to test the charge transfer resistance (R_{ct}) before and after electrochemical cyclic tests. Fig. 6a shows the equivalent circuit: R_s , R_f and R_{ct} are ohmic resistance (total resistance of the electrolyte, separator and electrical contacts), film resistance, and charge transfer resistance, respectively, and Z_w represents the Warburg impedance of Li ion diffusion into active materials. CPE is the constant phase-angle element, involving double layer capacitance.

The system resistance of R_s is similar for TiO_2 -400, TiO_2 -Ni-400 and TiO_2 -Mn-400 because of the fact that all the materials are coated directly on copper substrates that are used as current collectors, which ensures good electrical conductivity in the electrodes. Before the cycling, the total resistance of R_f and R_{ct} for three samples are in the order of TiO_2 -Ni-400 (110 Ω) > TiO_2 -Mn-400 (89 Ω) > TiO_2 -400 (80 Ω) (Fig. 6b). After cycling, the film resistance of R_f is similar for these three samples, the charge transfer resistance R_{ct} is in the order of TiO_2 -Mn-400 (57 Ω) > TiO_2 -400 (41 Ω) > TiO_2 -Ni-400 (29 Ω) (Fig. 6c), respectively. Before cycling, both doped samples exhibit higher resistance than the undoped one, which can be ascribed to the formation of a more complicated electrode/electrolyte interface induced by ion doping. After electrochemical cycling, TiO_2 -Ni-400 shows the lowest R_{ct} , which explains its high discharge capacity and good rate capability. To the opposite, TiO_2 -Mn-400's

charge transfer resistance R_{ct} is much higher than that of $\text{TiO}_2\text{-Ni-400}$'s after electrochemical tests. This explains well the different performance of Ni and Mn doped samples. Furthermore, all these three samples exhibit charge transfer resistance reduction after cycling, which can be ascribed to the electrode activation phenomenon after cycling [39].

Based on above results, we can summarize the effects of nickel ion doping on anatase TiO_2 as follows: during ion-exchange, Ni^{2+} ions replaced the removable H^+ in the protonated titanate, which would form a multi-structured TiO_2 . During calcination, the existence of Ni^{2+} ions induced an unit cell volume increase of the crystal structure and also caused lattice distortion, which would partially inhibit the growth of TiO_2 grains and cause less crystallinity. As a result, more lithium ions could be inserted into Ni-TiO_2 , justifying the high capacity during cycling. At the same time, Ni ions contributed to the formation of a more favorable electrode/electrolyte interface during cycling, as demonstrated in the EIS study. This interface facilitated the charge transfer process during lithium ion insertion and its existence explained why $\text{TiO}_2\text{-Ni-400}$ possessed a better rate capability than other samples.

4. Conclusions

In summary, an effective doping strategy was developed based on the ion-exchange process to obtain Ni-doped TiO_2 structures at room temperature. Compared to the undoped anatase TiO_2 , Ni ion doping improved the electrochemical performance of as-prepared TiO_2 notably when used as lithium ion battery electrodes. This enhancement can be ascribed to the effect of doped Ni ions on the TiO_2 structure,

including the inhibition of crystallinity under calcination, by causing lattice distortion. In addition, the introduction of Ni ions onto the surface of anatase TiO_2 structure contributed to the formation of a favorable electrode/electrolyte interface that reduced the charge transfer resistance significantly during repeated lithium ion insertion. All of these effects were achieved by a simple surface doping process. And the synthesis can be easily scaled up at room temperature. This proposed synthesis strategy would provide a novel and feasible doping method in the development of high performance materials used in lithium ion batteries and relevant fields.

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Figure captions

Fig. 1 Images of TiO_2 structures obtained after different processes: (a) SEM image of TiO_2 layered protonated titanate, (b) TEM image of TiO_2 layered protonated titanate, (c) SEM image of TiO_2 structure calcined at 400 °C for 3 h, and (d) SEM image of TiO_2 structure doped by nickel ions, and then calcined at 400 °C for 3 h.

Fig. 2 XRD patterns of different TiO_2 samples: (a) Protonated titanate fabricated at room temperature, the black line represents the blank sample holder, which has diffraction peaks of $2\theta \approx 16^\circ$ and 74° existing in all samples; (b) TiO_2 -400, TiO_2 -Ni-400 and TiO_2 -Mn-400.

Fig. 3 XPS spectra of TiO_2 samples: (a) TiO_2 -Ni-400 and (b) TiO_2 -Mn-400.

Fig. 4 Nitrogen sorption isotherms of TiO_2 -400, TiO_2 -Ni-400 and TiO_2 -Mn-400.

Fig. 5 Galvanostatic discharge (lithium insertion)/charge (lithium extraction) curves vs. Li^+/Li of TiO_2 -400, TiO_2 -Ni-400 and TiO_2 -Mn-400 cycled at a current of 30 mA g⁻¹ in the initial and last 3 cycles of a 50-cycle test (a-c), (d) Rate performances of all these three samples, measured at various rates with a voltage window between 1.0 and 2.5 V.

Fig. 6 The equivalent circuit used for fitting the experimental EIS data (a), Nyquist plots of TiO_2 -400, TiO_2 -Ni-400, and TiO_2 -Mn-400 before (b) and after cycling (c).

Figure 1a

Figure 1b

Figure 1c

Figure 1d

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4
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Figure 5a

Figure 5b

Figure 5c

Figure 5d

Figure 6a

a

Figure 6b

Figure 6c