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Mesoporous NaTi₂(PO₄)₃/CMK-3 nanohybrid as anode for long-life Na-ion batteries^{\dagger}

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In this work, a solvothermal strategy combined with following calcination was developed to synthesize a mesoporous $NaTi_2(PO_4)_3/CMK-3$ (NTP/C) nanohybrid as a high-performance anode for next-generation Na-ion batteries (NIBs). Physicochemical characterizations demonstrated that NASICON-type structured $NaTi_2(PO_4)_3$ (NTP) nanoparticles (NPs) with high crystallinity were homogeneously embedded in the mesoporous CMK-3 matrix. The mesoporous NTP/C nanohybrid as the anode for NIBs exhibited excellent electrochemical performance with high charge–discharge capability, good rate performance and long cycle life in non-aqueous electrolytes. The nanohybrid electrode delivered large specific capacities of 101, 76, 58, 39 mA h g⁻¹ at 0.2, 0.5, 1.0 and 2.0 C, respectively, and retained it as high as 62.9 mA h g⁻¹ even after 1000 cycles at 0.5 C. Compared to the pure NTP electrode, the mesoporous NTP/C hybrid anode with unique "meso–nano" architecture exhibited better Na-storage ability and indicated its promising application for rechargeable NIBs.

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Introduction

With the tremendous development of green and sustainable energies such as solar and wind power, it has become more and more important to seek and develop novel energy-storage systems with high energy density, power capability and round trip energy efficiency.¹⁻⁵ Recently, Li-ion batteries (LIBs) have been widely used in portable electronic devices, and would undoubtedly be considered as one desirable choice for electric vehicles (EVs), hybrid EVs, and even other large-scale energy storage equipments, due to their high energy density and long service life.⁶⁻⁸ However, the high cost and limited availability of lithium species have led to some great concerns over extensive applications of LIBs because of the low abundance and uneven distribution of lithium resources in the Earth's crust.^{2,9,10} On this background, sodium stands out and is well known as another cost-effective candidate to replace lithium, thanks to it being the fourth most abundant in nature and having similar physicochemical properties to those of lithium.^{11,12} As a result, rechargeable Na-ion batteries (NIBs) would be the best option for large-scale energy storage applications, where cycling life and cost are more essential factors than energy density, owing to the similar energy density and 'rocking-chair' sodium storage mechanism to those of LIBs, as well as the potentially low cost of sodium resources.^{13,14}

During the last few years, various materials as well as structure design processes currently applied for LIBs have been extended to advanced next-generation NIBs with large energy density, long life span, high efficiency, high safety and low cost.11-15 Recently, phosphates16-20 and fluorophosphates21-23 with a sodium insertion reaction mechanism have aroused much interest in NIBs. Since the first report on NIB in 1987, $NaTi_2(PO_4)_3$ (NTP) with a typical sodium super ion conductor (NASICON) structure was greatly established as one of the promising anodes in non-aqueous NIBs, benefiting from a redox potential (Ti⁴⁺/Ti³⁺) relative to the Na⁺/Na redox potential.²⁴ Moreover, the unique NTP with a typical NASICON-type structure presented a well-defined redox plateau ($\sim 2.1 \text{ V vs. Na}^+$ / Na) with two Na⁺ intercalation/deintercalation, delivering a high theoretical specific capacity of 132.8 mA h g^{-1} .^{20,25} Besides this, the NASICON-type phase, consisting of an open threedimensional (3D) framework of TiO₆ octahedra and PO₄ tetrahedra, generates large interstitial spaces, which provide structural stability and intrinsic safety even at high charge states due to its short Na-ion transport paths and strong covalent P-O

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[†] Electronic supplementary information (ESI) available: Synthesis of the mesoporous CMK-3; atomic coordinates, isotropic thermal parameters and occupation numbers for the NTP phase refined from X-ray powder diffraction data; WAXRD pattern of CMK-3; Raman spectrum of the mesoporous NTP/C nanohybrid and CMK-3; TG curve of the mesoporous NTP/C sample; FT-IR spectrum of the acid-treated CMK-3; FESEM images of CMK-3 and the mesoporous NTP/C nanohybrid; nitrogen sorption isotherms and PSD data of the mesoporous CMK-3; XRD pattern, Raman spectrum and TEM image of the pure NTP. See DOI: 10.1039/c4ta04732j

bond.^{25–28} However, similar to the case of lithium-ion batteries, the low insertion voltage involves the problems of solid electrolyte interphase (SEI) formation, which causes low coulombic efficiency (CE) and safety concerns.²⁹ The NASICON-type NTP phase, as a zero-strain insertion material similar to $Li_4Ti_5O_{12}$,^{30,31} has a relatively high Na insertion-deinsertion voltage plateau at ~2.1 V *versus* Na/Na⁺, which can avoid the formation of SEI and is very safe. As a result, these featuress make it a promising anode electrode material for large-scale long-life NIBs.

Unfortunately, the low intrinsic electrical conductivity of NTP itself is a major issue limiting its extensive application in high-performance NIBs, even if the open 3D framework of the NASICON-type structure is more beneficial for fast Na⁺ diffusion. For this reason, further smart modification of this material is necessary to improve its electrochemical performance, particularly at high rates. In order to address the drawback and improve the power performance of the NTP, two conventional methods have been put forward: (I) enhancing the electronic conductivity of NTP via combination with other highly conductive carbonaceous materials, especially with rich mesoporosity;19,20,25,28,32,33 (II) elegantly tailoring the particle size of electroactive NTP to reduce the ionic and/or electronic transporting path and increase the surface area. Recently, nanostructured NASICON-type hybrid materials have attracted interest because their large surface area increases the electrolyte/electrode contact area and a shorter path for Na⁺ and electron transport improves electrochemical kinetics. Therefore the hybrid nanostructure electrodes composed of carbon matrices and with controlled nanoparticle growth are potential materials both for rapid electronic and ionic transport, which are required for high rate performance. For example, NTP nanoparticles with size in the range of 100-400 nm after a carbon-coating treatment show enhanced electronic conductivity and high aqueous electrolyte ionic conductivity ($\sim 10^{-2}$ S cm⁻¹).²⁸ Mai et al. reported another NASICON-type structure, $Na_3V_2(PO_4)_3$ nanograins, with size ~ 5 nm distributed in different carbon matrices, which could increase the electrode/ electrolyte interfacial area and reduce the intercalation distance for Na⁺ and conductive pathways for electrons, and allow for efficient ion transport, thus improving the rate capability of NIBs.34

CMK-3, as a highly conductive mesoporous carbon with a high surface area (SSA), large pore volume, and ordered pore network, has attracted much attention for smart utilization of both as a conductive and porous matrix for energy storage applications.^{35–40} The unique mesoporous carbon cannot only increase the electrode/electrolyte interfacial area and the electrical conductivity, but allow for convenient ion transport, thus improving the electrochemical performance of the electrode.^{37–40} More attractively, one intriguing feature of CMK-3 is that it can serve as a conductive scaffold to efficiently encapsulate nanoscaled materials with a large naked surface to efficiently restrain the serious aggregation of the electroactive materials during long-term cycling.^{39,40}

In this work, we report a simple yet effective methodology for the fabrication of a mesoporous $NaTi_2(PO_4)_3/CMK-3$ (NTP/C) nanohybrid through a solvothermal method coupled with following calcination. Highly crystalline NTP nanoparticles (NPs) with an optimal size of \sim 5 nm were homogeneously embedded in unique mesopores of the CMK-3 matrix. It is the "meso-nano" feature of the NTP/C nanohybrid that facilitated entry of the electrolyte into the mesopores to get into contact with the embedded NTP nanocrystals and increased the electrolyte/electrode contact area for high Na-storage ability. Based on half-cell electrochemical tests, the NTP/C hybrid electrode delivered remarkable improvement of specific capacity, rate performance and cycling stability, compared to the pure NTP phase, benefiting from the advantages of its appealing structure.

Experimental

Synthesis of materials

CMK-3 was prepared using SBA-15 as a template, and a more detailed synthesis is described in the ESI[†]. The mesoporous NTP/C nanohybrid was prepared by a solvothermal method by using benzyl alcohol (BA) as the surfactant. In brief, 0.3 g of CMK-3 powder was first refluxed in 6 M HNO₃ under stirring for 1 h at 80 °C to induce hydrophilicity. Then, 0.2 g of acid-treated CMK-3 was dissolved into a solution containing 25 mL of ethylene glycol and 15 mL of BA under continuous stirring and sonication for 1 h, respectively. Next, 10 mL of ammonia solution (28 wt%) and 3.4 mL of tetrabutyl titanate were added dropwise to the above solution. After vigorous stirring for 10 h, 1.7255 g of NH₄H₂PO₄ in 10 mL of deionization (DI) water and 0.265 g of Na₂CO₃ in 10 mL of DI water were added, respectively. The resultant gray gel mixture was stirred for 5 h, then transferred into an 80 mL Teflon-lined stainless steel autoclave, and further treated at 140 °C for 48 h. The obtained product was washed with DI water and ethanol several times, respectively. After drying at 80 °C, the products were ground and sintered at 700 °C for 2 h at a heating rate of 2 °C min⁻¹ in a N₂ atmosphere.

Characterization of materials

Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer (Cu Ka radiation, 40 mA, 40 kV). The XRD profiles were refined by the Rietveld program RIETAN-FP.41 Schematic illustrations of the crystal structures were drawn using the program VESTA.42 Raman spectra were recorded on a Renishaw 2000 system with an argon ion laser (514.5 nm) and a charge-coupled device detector at room temperature. Thermogravimetric (TG) analysis was performed on a TG instrument (NETZSCH STA 409 PC) at a heating rate of 5 °C min⁻¹ in an air atmosphere from 50 °C to 800 °C. The Fourier-transform infrared (FT-IR) spectrum was obtained using an FT-IR spectrometer (Jasco, FT-IR-4100, Japan) under transmission mode based on the KBr pellet method in the range of 450–2000 cm⁻¹. Morphologies and structures were observed by field-emission scanning electron microscopy (FESEM, Nova Nano SEM 430, FEI), transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) (JEM-2100, JEOL). N_2 adsorption-desorption was analyzed *via* BET measurements by using an ASAP-2010 surface area analyzer.

Electrochemical measurements

The electrodes were fabricated using a mixture of the prepared NTP/C (80 wt%), carbon black (10 wt%), and polyvinylidene fluoride (PVDF 10 wt%) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The pure NTP electrode was prepared by mixing 70 wt% active material, 20 wt% carbon black and 10 wt% PVDF in NMP. The slurry was then spread uniformly onto a Cu foil current collector which was prepared by punching the electrode film into circular pieces with a diameter of 12 mm, and then dried in an oven at 110 °C for 24 h under vacuum. The loading mass of the active material in the electrode was around 2 mg. Electrochemical performance was tested by assembling CR2032-type coin cells in an argon-filled glove box, using Na foil as the counter electrode and a glass fibre as the separator. 1 M NaClO₄/ethylene carbonate (EC) and propylene carbonate (PC) (1:1 in volume) was used as the electrolyte. The galvanostatic charge-discharge (GCD) experiment was performed under different current densities between 1.0 and 3.0 V (vs. Na⁺/Na) using a CT2001A cell test instrument (LAND Electronic Co.). Cyclic voltammetry (CV) tests of the cells were carried out on a CHI 660E electrochemical workstation. The AC impedance spectrum was measured using the electrochemical workstation in the frequency range 10^{-2} to 10^{6} Hz.

Results and discussion

Synthesis and structural analysis of the mesoporous NTP/C nanohybrid

Herrin, CMK-3 was firstly synthesized by the replication of mesoporous silica SBA-15, as reported previously.⁴³ The resulting CMK-3 was then treated with 6 M HNO₃ to introduce some functional groups, such as –OH and –COOH, on its surface to make it hydrophilic for the following impregnation in the aqueous solution.⁴⁴ After that, the pretreated CMK-3 was immersed in the precursor solution for the following solvothermal treatment. The final product, NTP-impregnated CMK-3 powder, was further sintered at 700 °C just for 2 h in a N₂ atmosphere.

Fig. 1a shows the Rietveld refinement of the wide-angle X-ray diffraction (WAXRD) pattern for the mesoporous NTP/C nanohybrid. It confirms the well-crystallized NASICON-type NTP, corresponding to the rhombohedral space group: $R\bar{3}c$ (167). Moreover, all refinements gave a small value of factors including $R_{\rm wp}$, $R_{\rm p}$ and S, indicative of a good and reliable structural analysis (Table S1†). The hexagonal cell lattice parameters were found to be a = 8.4884(4) Å and c = 21.812(1) Å from the refinement, very close to the values reported before.⁴⁵ Meanwhile, a very broad diffraction peak at $2\theta = 25.2^{\circ}$ was observed in the WAXRD pattern (the inset in Fig. 1), which is contributed by the high-content and noncrystalline graphite phase of CMK-3. It can be further confirmed by the WAXRD pattern of CMK-3 (Fig. S1†). Evidently, it could be seen that no



Fig. 1 Rietveld refinement (a) of the XRD pattern for the mesoporous NTP/C nanohybrid; the inset in (a) shows the magnification of the black-rectangle region, crystal structure (b) of the NTP phase at different orientations, FT-IR spectrum (c) of the NTP/C sample recorded in the range of $450-4000 \text{ cm}^{-1}$, and small-angle XRD pattern (SAXRD) (d) of the mesoporous NTP/C nanohybrid product; the inset in (d) shows the SAXRD pattern of the original CMK-3.

diffraction peaks corresponding to the crystalline graphite phase were found in the XRD pattern of CMK-3, strongly suggesting the amorphous nature of the as-fabricated CMK-3. This has been further confirmed by a Raman spectroscopy measurement as evidenced by the appearance of disordered amorphous carbon (D band) and crystalline graphic carbon (G band) in the Raman spectrum of the mesoporous NTP/C nanohybrid (Fig. S2[†]). The relative intensity of the D-band to Gband $(I_{\rm D}/I_{\rm G})$ value confirms that CMK-3 exhibits characteristics of nanocrystalline carbon with a low and close degree of graphitization.⁴⁶ Thermogravimetric (TG) analysis was applied to determine the specific content of CMK-3 in the resulting NTP/ C hybrid. As estimated from the TG data (Fig. S3[†]), the content of carbon existing in the nanohybrid was approximately 11.9 wt%. Also notably, except for the crystalline NTP and amorphous CMK-3, no other parasitic phases could be detected, revealing that CMK-3 has no influence upon the formation of NASICON-type NTP.

Schematic illustration of the NASICON-type NTP structure obtained from the resulting Rietveld refinement parameters is displayed in Fig. 1b. The rhombohedral NTP possesses an open 3D framework consisting of TiO₆ octahedra and PO₄ tetrahedra, well known for its facile Na⁺ migration, which has been well documented.^{19,20,25,28,32,33} In the structure, 2 TiO₆ octahedra are separated by 3 PO₄ tetrahedra and they share all their corner oxygens to construct the framework anion of $[Ti_2(PO_4)_3]^-$ units in the *c*-axis direction. The $[Ti_2(PO_4)_3]^$ framework has two types of interstitial sites: one (A1) is in the elongated octahedral oxygen environment at the intersection of three conduction channels, and the other (A2) is close to A1 and in the three 8-coordinate site environment at each bend of the conduction channels.^{26,27} As for the NTP phase, Na⁺ preferably occupies octahedral A1 site. During transport, Na-ions actually occupy octahedral A2 site, forming the unique NTP phase.47,48

Formation of the mesoporous NTP/C nanohybrid is also confirmed by an FT-IR analysis and the representative spectrum is displayed in Fig. 1c. The FT-IR data shown in Fig. 1c are in good agreement with Pet'kov's work.49 The vibrations from Ti4+- O^{2-} bonds of TiO₆ octahedra are evident at 644 and 997 cm⁻¹, respectively. The presence of P-O bonds in PO₄ tetrahedra is detected at 572 and 1022 cm⁻¹. The infrared bands in the range of 1150–1250 cm⁻¹ can be attributed to the stretching vibration of PO₄ units. In addition, the bands at 1606 and 3411 cm^{-1} , characteristic of the presence of -COOH and -OH hydroxyl groups, respectively, have been observed. They should be ascribed to the functionalities in pretreated CMK-3,50 which are also evident in the corresponding FT-IR spectrum of the pretreated CMK-3 (Fig. S4[†]). The combined data observed in XRD and FT-IR, as presented above, strongly confirm the rhombohedral NASICON-type structure characteristic of NTP in the mesoporous nanohybrid.

Representative SAXRD patterns for the CMK-3 and NTP/C nanohybrid are both illustrated in Fig. 1d. As seen from the inset in Fig. 1d, the three peaks can be indexed successfully to the (100), (110), and (200) reflections of the 2D hexagonal mesostructure (space group *P6mm*) of the mesoporous CMK-3, suggesting its long range regularity and highly ordered nature.³⁹ As regards the mesoporous NTP/C nanohybrid, it could be seen that the (110) and (200) diffraction peaks almost disappear after impregnation with NTP NPs, which indicates that the ordered channels of CMK-3 are partially destroyed due to filling effects during the following impregnation process.⁴⁰

CMK-3 presents micrometer-sized rod-like architecture with length in the range of 20-30 µm, which consists of numerous worm-like mesoporous structures, as observed in FESEM images (Fig. S5a and b[†]). As seen from Fig. 2a and b, ordered mesoporous channels with a uniform size in CMK-3 are revealed, and they are assemblies of hexagonally ordered carbon nanorods (CNRs) separated by mesoscale porous channels, in which the individual CNRs are interconnected by carbon spacers. This result is consistent with the SAXRD pattern (the inset in Fig. 1d) of CMK-3, and the findings in ref. 35 and 36. After impregnation with the sodium titanium oxide precursor and solvothermal treatment coupled with the following high-temperature calcination, worm-like mesoporous structures no longer aggregate, and form micrometer-sized rodlike particles (Fig. S5c and d[†]). HRTEM was further used to investigate the dispersion of NTP NPs in the mesoporous CMK-3 matrix. As demonstrated in Fig. 2c, lots of NTP/C NPs with a size in the range of several nanometers to several tens of nanometers were uniformly distributed both inside and outside the mesoporous channels. Fig. 2d presents a HRTEM image of another NTP/C nanohybrid bundle, in which NTP/C NPs are embedded in mesopore channels of the carbon matrix and the size of the NPs is estimated as ~ 5 nm with high crystallinity. The lattice fringes with interplanar distances of 0.348 and 0.366 nm are in keeping with the *d*-spacing of the (202) and (113) planes of the NASICON-type NTP phase, respectively. For further investigation of the distribution of NTP NPs and CMK-3, a bright field STEM image and elemental mapping of the corresponding region are shown in Fig. 2e, indicating spatial



Fig. 2 TEM images (a and b) of CMK-3, HRTEM images (c and d) of the resultant mesoporous NTP/C nanohybrid and bright-field STEM image (e) of NTP/C, elemental mapping of the same region, indicating the spatial distribution of C, P, O, Ti and Na elements, respectively.

distribution of C, O, P, Ti and Na elements, respectively. O, P, Ti and Na were uniformly distributed in the rod-like CMK-3 and the EDS mapping images of these elements overlapped with each other. Meanwhile, the distributions of these chemical elements were in the range of the EDS mapping of C, which were consistent with the target mesoporous NTP/C nanohybrid structure. It should be noted that the EDS image of C element does not show a similar rod-like architecture under the influence of carbon support films. These results strongly demonstrate that the acid-treated CMK-3 plays a significant role in controlling the morphology by acting as the nucleation site for efficient deposition through strong interaction between the oxygen-containing groups and other metal ions. Meanwhile, the mesoporous structure of the NTP/C nanohybrid perfectly provides a convenient and fast transportation channel for Na⁺, and increases the electrolyte/electrode contact area.39,40

Specific surface area (SSA) and pore size distribution (PSD) were used to investigate both CMK-3 (Fig. S6†) and the mesoporous NTP/C nanohybrid (Fig. 3) in detail by using nitrogen isothermal adsorption–desorption measurement. Obviously, both samples display typical type IV isotherms of a mesoporous structure. As evident from the isothermal adsorption–desorption spectrum (Fig. S6a† and 3a), it was found that the SSA significantly decreases from $1311 \text{ m}^2 \text{ g}^{-1}$ (CMK-3) to $152 \text{ m}^2 \text{ g}^{-1}$ (NTP/C) after NTP incorporation into the CMK-3 matrix. The



Fig. 3 Nitrogen sorption isotherm (a) and PSD (b) of the mesoporous NTP/C nanohybrid.

sharp decrease in SSA should be ascribed to the filling of mesopores existing in the nanohybrid. The PSDs of the mesoporous NTP/C nanohybrid and CMK-3 are shown in Fig. 3b and S6b,† respectively. Clearly, CMK-3 has an average pore size of ~6.9 nm, while the NTP/C nanohybrid possesses a PSD with an average size of ~5.3 nm. The smaller mesopores in the nanohybrid indicate that the NTP nanocrystals are uniformly embedded in the pores of the CMK-3 matrix.

Electrochemical performance

The electrochemical performance of the mesoporous NTP/C nanohybrid as an anode electrode material in sodium half-cells was evaluated by CV and GCD cycling. For comparison, pure NTP NPs were also prepared in a manner similar to that of the mesoporous NTP/C nanohybrid, just with the exception of the absence of CMK-3 in the process. The XRD pattern, Raman spectrum and TEM image of pure NTP (Fig. S7†) show the highly crystalline NASICON-type NTP phase (JCPDC no. 85-2265) without any other impurities, and irregular sub-micrometer particle aggregates of 50–200 nm. Fig. 4a shows the CV curves of the NTP/C nanohybrid electrode for the first three cycles at a scan rate of 0.1 mV s⁻¹. A pair of well-defined sharp redox peaks located at 2.09 (red.) and 2.16 V (ox.) (ν s. Na⁺/Na) are observed, where the peak shape and potential position remain almost



Fig. 4 CV curves (a) in a voltage range of 1.5 to 2.8 V (vs. Na⁺/Na) of the NTP/C electrode at a scan rate of 0.1 mV s⁻¹, the first three charge–discharge profiles (b) of the NTP/C electrode at 0.2 C, GCD plots of NTP/C (c) and pure NTP (d) anodes at various C-rates.

unchanged during successive scans, suggesting good cycling stability of the nanohybrid material in a non-aqueous electrolyte. This pair of CV peaks could be attributed to the redox reaction of Ti^{4+}/Ti^{3+} , respectively, indicating the reversible insertion–extraction reaction of Na^+ in the NTP lattice for the reaction, as depicted by the following equation:^{19,20,28}

$$NaTi_2(PO_4)_3 + 2Na^+ + 2e^- \leftrightarrow Na_3Ti_2(PO_4)_3.$$

According to the reaction, the theoretical capacity of the NTP phase is 132.8 mA h g⁻¹. The initial three charge–discharge profiles of the mesoporous NTP/C nanohybrid electrode in the potential voltage window of 1–3 V vs. Na⁺/Na at a rate of 0.2 C (1 C = 132.8 mA h g⁻¹) are shown in Fig. 4b. The initial charge–discharge capacities of this material are 102 and 100 mA h g⁻¹ respectively, corresponding to a 75% utilization of its theoretical 2 Na⁺ insertion–extraction capacity with a high CE of 98%. Such a high initial efficiency was seen for the Na insertion reaction for the NASICON-type structured material previously reported,^{28-30,34} suggesting an excellent electrochemical reversibility of NTP/C for NIBs. Due to the activation of the electrode material, the CE is not high in the beginning, but still could reach ~100% after a few cycles.

The GCD curves of the mesoporous NTP/C nanohybrid electrode at different C-rates in the second cycle were evaluated, and the results were compared with the pure NTP sample, as shown in Fig. 4c and d. Strikingly, the mesoporous NTP/C nanohybrid is able to deliver much higher discharge-charge capacities, compared to pure NTP at the same rate. For example, the nanohybrid anode delivers a large discharge capacity of 102 mA h g^{-1} at a rate of 0.2 C, while the discharge capacity of the pure NTP electrode is only 35.1 mA h g^{-1} at 0.2 C. Besides this, the former has a distinct charge-discharge voltage plateau at a high current rate of 2 C, while no clear charge-discharge voltage plateau is presented for the latter even at a low rate of 0.2 C. The distinct difference reveals that the nanohybrid anode exhibits fast Na⁺ insertion-extraction kinetics, for which the mesoporous feature and good electrical conductivity of the hybrid architecture, and the nanoscale size of the impregnated NTP could be responsible.39,40

The rate and cycling performances of the mesoporous NTP/C nanohybrid and the pure NTP electrodes were examined at various charge-discharge rates from 0.2 to 2 C, and each sustained for 5 cycles, as illustrated in Fig. 5. In contrast to the pure NTP electrode, the nanohybrid exhibits higher specific capacities and better rate performances. As observed in Fig. 5, the mesoporous NTP/C nanohybrid anode demonstrates rate performance with reversible charge–discharge capacity of \sim 101 mA h g⁻¹ at 0.2 C, \sim 76 mA h g⁻¹ at 0.5 C, \sim 58 mA h g⁻¹ at 1.0 C and \sim 39 mA h g⁻¹ at 2.0 C, respectively, while the pure NTP electrode can only deliver discharge specific capacities of \sim 34, \sim 19, \sim 10, \sim 3 mA h g^{-1} at 0.2, 0.5, 1.0 and 2.0 C, respectively. Moreover, the reversible charge-discharge capacity of the mesoporous NTP/C hybrid anode can return to \sim 88 mA h g⁻¹ when the charge–discharge rate is suddenly changed back to 0.2 C after 20 cycles. This result demonstrates that the mesoporous nanohybrid anode is tolerant



Fig. 5 Rate and cycling performances of the mesoporous NTP/C nanohybrid and pure NTP electrodes.

to varied charge–discharge current and the capacity can even recover to the original value as long as the current reverses back to the low rates.

Based on the results mentioned above, the mesoporous NTP/C nanohybrid and pure NTP electrodes were further investigated for the long-term GCD cycling at a rate of 0.5 C. Both of them exhibited excellent cyclic stability performance, as shown in Fig. 6a. The discharge capacity of the nanohybrid electrode is as high as 74.5 mA h g^{-1} at the 200th cycle, and after 1000 charge-discharge cycles, the capacity still remains at \sim 62.9 mA h g⁻¹. Therefore, the capacity-decay rates of the hybrid anode amounts to approximately 0.014% per cycle at 0.5 C, calculated from the 800 cycles. In addition, the electrode also maintains high CE with an average value of 99.9% and the average specific discharge capacity is \sim 70.9 mA h g⁻¹ at 0.5 C over 1000 cycles. Moreover, the CE of the pure NTP electrode also delivers an average value of 99.9% over 500 cycles even though it exhibits very low specific capacity with an average discharge capacity of \sim 13.1 mA h g⁻¹.



Fig. 6 Long-term charge–discharge cycling performance (a) of the mesoporous NTP/C nanohybrid and pure NTP electrodes at a current rate of 0.5 C, XRD (b), TEM (c) and HRTEM (d) images of the mesoporous NTP/C nanohybrid electrode after 1000 cycles at a rate of 0.5 C.

After 1000 cycles at 0.5 C, the XRD pattern of the NTP/C electrode was studied to confirm its stability. As can be seen in Fig. 6b, the NTP/C anode after long-term cycles still remained in the wellcrystallized rhombohedral NaTi₂(PO₄)₃ phase (JCPDS no. 85-2265) with a = 8.4935(8) Å and c = 21.807(7) Å. Compared to the lattice parameter of the mesoporous NTP/C nanohybrid before the charge-discharge cycles, the NTP phase operates based on the insertion-deinsertion reaction without significant volume expansion, which enables stable cycle performance similar to Li₄Ti₅O₁₂.^{30,31} However, typical diffraction peaks of Cu were observed in the XRD pattern of the NTP/C electrode material. This was because the electrode material spread uniformly onto the Cu foil current collector. Meanwhile, the specific architecture of the mesoporous NTP/C nanohybrid was also examined by HRTEM, as displayed in Fig. 6c and d. Impressively, the nanohybrid maintains the previous morphological features of NTP NPs with a size of ~ 5 nm, which are still homogeneously embedded in the mesoporous channels of the carbon matrix. Besides, the SEI film is non-existent on the surface of NTP NPs, which can be clearly confirmed by HRTEM inspection (Fig. 6d). This result is also consistent with absence of the irreversible capacity after the 1st cycle in Fig. 4b and 5a. Both the cyclic stability and the morphology of the NTP/C sample after 1000 charge-discharge cycles demonstrate that the perfectly crystalline NTP NPs embedded in mesoporous channels formed a stable structure on the microscale, and the electrochemical Na⁺ insertion-extraction reaction was highly reversible.

To further establish the relationship between electrochemical performance and electrode kinetics for the mesoporous NTP/C nanohybrid and pure NTP electrodes, Nyquist plots from AC impedance spectroscopy measurements were collected on fresh cells (Fig. 7). The impedance spectra of both electrodes consist of a single depressed semicircle in the high frequency region and an inclined line at low frequency, corresponding to the charge-transfer resistance (R_{ct}) and the solidstate diffusion of ions in the active materials, respectively. The NTP/C electrode shows semicircles of a smaller diameter in the Nyquist plots than those of the corresponding pure NTP electrode, indicating lower R_{ct} and better kinetics for Na⁺ insertion reactions. This result clearly implies that the electronic conductivity of NTP has been remarkably improved due to the presence of CMK-3.



Fig. 7 Nyquist plots of the mesoporous NTP/C nanohybrid and pure NTP electrodes in newly assembled test cells.

Conclusions

In summary, we reported a simple solvothermal strategy coupled with following calcination to fabricate a mesoporous NTP/C nanohybrid architecture, in which NASICON-type NTP NPs were homogeneously embedded in a mesoporous CMK-3 matrix. Herein, CMK-3 not only acted as a rigid support for the NTP NPs, preventing serious agglomeration and growth of NTP nanocrystals during calcination and continuous cycling, but also created a conductive and interconnected carbon matrix, providing high electronic conductivity and mesoporous structure for both facile charge and mass transfer. Benefiting from the good conductivity, high surface area and the good stability of the mesoporous NTP/C nanohybrid, the unique hybrid anode was endowed with high charge-discharge capacity, good rate performance and long cycle life based on half-cell testing. More importantly, the electrode architecture design developed here might open avenues to promising materials for advanced NIBs for high performance large-scale energy storage devices.

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