The binder-free Ca$_2$Ge$_7$O$_{16}$ nanosheet/carbon nanotube composite as a high-capacity anode for Li-ion batteries with long cycling life†

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We report a facile one-step route to synthesize a Ca$_2$Ge$_7$O$_{16}$ nanosheet (NS)/carbon nanotube (CNT) anode for the first time. The Ca$_2$Ge$_7$O$_{16}$ NS/CNT composites are uniformly grown on the surface of three-dimensional Ni foam used as the conductive current collector. The Ca$_2$Ge$_7$O$_{16}$ NS/CNT composite is used as a binder-free anode for lithium-ion batteries, which delivers a reversible capacity of 998.5 mAh g$^{-1}$ at a current rate of 0.5 A g$^{-1}$ and exhibits excellent cycle performance (87% retention of its 2nd cycle reversible capacity after 1000 cycles). Furthermore, a binder free full cell is fabricated, which shows excellent cycle performance with 96% retention of its 10th cycle capacity after 100 cycles. The superior cycling performance is attributed to the synergetic effect of small diffusion lengths in NS, sufficient void space to buffer the volume expansion, the CNT for charge transport and a continuous 3D electronic path of the Ni foam.

Introduction

Lithium-ion batteries (LIBs) have been widely utilized in portable electronic devices, electric vehicles and power tools, because of their high energy density, high rate capability, high safety and low cost.$^{1,2}$ However, commercial graphite materials used as the anode materials of lithium-ion batteries have a low theoretical capacity (372 mAh g$^{-1}$), which limits the application of LIBs.$^{1,5}$ From the viewpoint of energy density, group IVA elements are the most promising materials, especially Si and Ge, which can deliver theoretical capacities of 4200 mA h g$^{-1}$ with Si-based materials, Ge exhibits a higher diffusion coefficient of 6.572 (versus 1.389 for Si) and higher intrinsic electrical conductivity (100 times higher than Si).$^{6}$ Compared with Si-based materials, Ge exhibits a higher diffusivity of lithium (400 times faster than Si), a lower specific volume change and high intrinsic electrical conductivity (100 times higher than Si) during the Li insertion/extraction process, which can be expected to lead to a better cycling performance at comparable capacity.$^{7,8}$ However, Ge still undergoes a volume change of 370%.$^9$ To minimize such volume strain during the charge and discharge processes, we have devoted to creating germanium nanostructures that can accommodate the lithiation-induced strain and thus exhibit high coulombic efficiency and long cycle life.$^{10-12}$

Another issue that must be addressed here is the problem of feasibility as Ge is not an abundant or inexpensive material.$^{13}$ Despite its advantages, Ge has received less attention than the more widely investigated Si, mainly because of its high cost.$^{14}$ Therefore, to discover a stable and high capacity Ge-based compound, earth-abundant elements would be the best solution to cover all problems mentioned above. In recent years, ternary Ge compounds (MGEO$_x$, where M = Cu, Fe and Co) electrodes are regarded as promising anodes for LIBs, which generate nanosized metallic M particles that make an intimate contact with the nano-sized Ge (CuGeO$_3$ + 2Li$^+$ + 2e$^-$ → Cu + Li$_2$O + GeO$_2$, 2GeO$_2$ + 4Li$^+$ + 4e$^-$ → Ge + 2Li$_2$O) and Li$_2$O, that they can catalyze Li$_2$O decomposition (Ge + 2Li$_2$O → GeO$_2$ + 4Li$^+$ + 4e$^-$) and provide an electronic conductive network for Ge oxidation.$^{15}$ From then on, germanate containing metal elements (Zn,$^{15,16}$ Cu,$^{17}$ Ba,$^{18}$ Sr,$^{18}$ Cd,$^{19}$ Fe$^{20}$) have been reported for lithium storage. Ca$_2$Ge$_7$O$_{16}$ has demonstrated its promising potential for applications in high performance LIBs for low-cost, environmentally benign, and good stabilized matrix.$^{14,18,21,22}$ The CaO formed in situ (CaO for Ca$_2$Ge$_7$O$_{16}$) after the initial delithiation process, accompanied by the formation of Li$_2$O, can not only serve as a buffer matrix to accommodate the volume changes in the germanium nanoparticles, but also effectively prevent the agglomeration of the nanosized germanium particles that are formed during the process. For example, Guo et al.$^{18}$ showed the better cycling performance of Ca$_2$Ge$_7$O$_{16}$ that can be expected to lead to a better cycling performance.

†Electronic supplementary information (ESI) available: Crystal structure of the Ca$_2$Ge$_7$O$_{16}$, TG results, N$_2$ adsorption–desorption, discharge–charge profiles, SEM and a simple application of a Ca$_2$Ge$_7$O$_{16}$ NS/CNT composite. See DOI: 10.1039/c6ra14289c

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nanowires with a specific capacity of 601 mA h g$^{-1}$ after 100 cycles under a current density of 100 mA g$^{-1}$ than BaGe$_2$O$_5$ nanowires and GeO$_2$. However, the coulombic efficiency (CE) in the first cycle of Ca$_2$Ge$_7$O$_{16}$ nanowires is 18.1%, which is lower than BaGe$_2$O$_5$ nanowires (25.6%) and GeO$_2$ (33%). Shen et al. showed improved cycling performance of the Ca$_2$Ge$_7$O$_{16}$ nanowires/graphene anodes with a specific capacity of 950 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ after 100 cycles and a higher CE (45%). The Ca$_2$Ge$_7$O$_{16}$ hollow microspheres which were prepared by Guo et al. exhibited the superior electro-chemical properties with a specific capacity of 804.6 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ after 100 cycles and the CE was less than 50%. However, these Ca$_2$Ge$_7$O$_{16}$ electrodes had relatively low CE and short cycling life under a lower current density (100 mA g$^{-1}$) due to the pulverization caused by the volume expansion and poor electronic conductivity. Therefore, the synthesis of Ca$_2$Ge$_7$O$_{16}$ with well-defined nanostructures and excellent lithium storage capacity remains a great challenge owing to the volume expansion of Ca$_2$Ge$_7$O$_{16}$.

The NS electrodes have shown many advantages, such as good electrical conductivity, low diffusion resistance to ionic species, easy electrolyte penetration, and large electroactive area. Synthesis of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT electrode and the commercial LiCoO$_2$ were obtained. In a typical procedure, 30 mg acid-treated CNTs were refluxed in a mixed solution of concentrated HNO$_3$ and H$_2$SO$_4$ overnight to open the CNTs tips. After filtering, washing with pure water and drying, the open CNTs were obtained. Then a piece of cleaned Ni foam was placed into the solution. The mixture was stirred for 60 min and then transferred to a Teflon-lined auto-clave with a 100 mL inner volume. Then a piece of cleaned Ni foam was placed into the solution. The hydrothermal synthesis was performed at 180 °C for 20 h, followed by natural cooling to room temperature. The white product was collected by centrifugation, washed thoroughly with water and alcohol several times and then dried at 60 °C in air for 12 h. Finally, the Ca$_2$Ge$_7$O$_{16}$ NS Ni foam was obtained.

From Shanghai Longjin Metallic Material Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd. of China, respectively. High purity CNTs (20–30 nm) were purchased from Beijing Boyu New Material Co., Ltd. Ni foam and commercial LiCoO$_2$ were purchased from Shenzhen Biiyuan Electronic Co., Ltd.

**Synthesis of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT**

CNTs were refluxed in a mixed solution of concentrated HNO$_3$ and H$_2$SO$_4$ overnight to open the CNTs tips. After filtering, washing with pure water and drying, the open CNTs were obtained. In a typical procedure, 30 mg acid-treated CNTs were dissolved in 30 mL deionized water, respectively. The mole ratio of Ca : Ge is 2. The Ca(CH$_3$COO)$_2$·H$_2$O solution was added dropwise to GeO$_2$ solution under vigorous stirring. The mixture was stirred for 60 min and then transferred to a Teflon-lined auto-clave with a 100 mL inner volume. Then a piece of cleaned Ni foam was placed into the solution. The hydrothermal synthesis was performed at 180 °C for 20 h, followed by natural cooling to room temperature. The white product was collected by centrifugation, washed thoroughly with water and alcohol several times and then dried at 60 °C in air for 12 h. Finally, the Ca$_2$Ge$_7$O$_{16}$ NS Ni foam nanocomposite was obtained.

**Characterization**

The morphology and element distribution of the electrodes were investigated by field emission-scanning electron microscopy (FE-SEM; Hitachi S-4800) operating at 20 kV. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2F30 operated at 300 kV. X-Ray Diffraction (XRD) measurements were performed at a Rigaku D/max-rB X-ray diffractometer with Cu Kz ($\lambda = 0.1548$ nm) incident radiation. The diffraction patterns were collected at room temperature in the 2θ ranges of 10 to 90°. Raman spectroscopy was performed with a laser micro Raman spectrometer (RenishawVia, Renishaw, 532 nm excitation wavelength). An X-ray photoelectron spectroscopy (XPS) study was conducted with a PHI 5700 ESCA System using Al Kz radiation (1486.6 eV). Thermogravimetric (TG) analysis was performed on a SDT Q 600 V 20.9 Build 20 TG/DTA apparatus at a heating rate of 10 °C min$^{-1}$ in flowing air.
Brunauer–Emmett–Teller (BET) analysis was carried out using a N₂ adsorption–desorption apparatus (3H-2000PS1, BASS).

Electrochemical charge–discharge behaviors were investigated in stimulant cells (2032 coin-type half-cells) assembled with Ca₂GeO₁₆ NSs/CNTs composite as the positive electrode (cathode), a Li metal foil as the negative electrode (anode), a separator film (Celgard 2400), and a liquid electrolyte (ethylene carbonate and dimethyl carbonate (1 : 1 by volume)) with 1.0 M LiPF₆ in an Ar filled glove box. The loading density of the Ca₂GeO₁₆ NS/CNT active materials was calculated to be 1.0–2.0 mg cm⁻². Each cell was aged for 24 h at room temperature before commencing the electrochemical tests. The galvanostatic charge–discharge measurements were conducted in a battery test system (NEWARE BTS-610, Newware Technology Co., Ltd., China) at room temperature. The cut-off voltage for all tests was 0.01–3.0 V. A full cell was assembled by using the as-fabricated Ca₂GeO₁₆ NSs/CNTs as the anode, commercial LiCoO₂ as the cathode, LiPF₆ as the electrolyte, and a polymer separator. The electrochemical tests were cycled between 2.0 and 4.2 V for the complete anode-limited full cells at a constant current density of 200 mA g⁻¹ with respect to the mass of the anode. Cyclic voltammograms (CV) were measured at a scan rate of 0.1 mV s⁻¹ for 5 cycles on an electrochemical work station (CHI660E). AC impedance of the half-cells was also measured at a frequency range of 100 mHz to 100 kHz. All testing was performed at room temperature.

**Results and discussion**

The synthetic process of the Ca₂GeO₁₆ NSs/CNTs nanocomposite is schematically illustrated in Fig. 1. Firstly, HGeO₃ was formed from the reaction of GeO₂ and OH⁻ which came from CH₂COO⁻. Then free Ca²⁺ ions which derived from Ca(CH₂COO)₂·H₂O reacted with HGeO₃⁻, and finally the Ca₂GeO₁₆ nuclei generated on Ni foam (Fig. 1a). As the reaction time prolonged, the Ca₂GeO₁₆ nuclei started to assemble along the specific orientation preferentially and formed the Ca₂GeO₁₆ NS (Fig. 1b). The CNTs were adhered on the surface of the Ca₂GeO₁₆ NSs through electrostatic interaction to form the Ca₂GeO₁₆ NS/CNT nanocomposites.

The crystalline structure of the Ca₂GeO₁₆ NS/CNT nanocomposite was characterized by XRD and the results are shown in Fig. 2a. All of the diffraction peaks can be well indexed to the orthorhombic phase of Ca₂GeO₁₆ (JCPDS Card no. 34-0286). Diffraction peaks which might appear for the CNTs are absent; most likely the CNT peaks are eclipsed by those for Ca₂GeO₁₆.

The crystallographic structure of the orthorhombic Ca₂GeO₁₆ is shown in Fig. S1.† Fig. 2b shows Raman spectrum of the Ca₂GeO₁₆ NS/CNT nanocomposite. The characteristic D band and G band of the Ca₂GeO₁₆ NS/CNT are observed at 1349.4 cm⁻¹ and 1583.1 cm⁻¹, respectively. The D-band is commonly assigned to a breathing mode of A₁g symmetry that involves phonons near the K-zone boundary, and the G-band corresponds to the zone center E2 mode which is related to phonon vibrations in sp² carbon materials. Fig. S2† shows the carbon content in the Ca₂GeO₁₆ NS/CNT nanocomposite is evaluated to be ca. 19.5% by TG analysis. Fig. 2c shows the general XPS spectrum of the Ca₂GeO₁₆ NS/CNT nanocomposite, which includes the elements C, Ge, Ca and O. The C 1s spectrum (Fig. 2d) could be divided into four peaks corresponding to the C–C (sp² C), C–O, C=O, and O=C=O groups at 284.5, 285.3, 286.4 and 290.7 eV, respectively. As shown in Fig. S3,† the peak at 32.1 eV is assigned to Ge 3d, indicating that Ge in the sample exists in the form of Ge⁴⁺ before the cycle.²⁸

Fig. 3 shows the morphology the Ca₂GeO₁₆ NS/CNT nanocomposite supported on the Ni foam. It reveals that a large number of Ca₂GeO₁₆ NS/CNT nanocomposites with the thickness ranging from 20–40 nm grow vertically and uniformly on the Ni foam, forming an interconnected and highly porous configuration. CNTs with the length of about 50–150 nm are well distributed on the surface of the Ca₂GeO₁₆ NSs. The porous structure of the composite was further evaluated by BET N₂-adsorption–desorption analysis (Fig. S4†). Such NS structure gives rise to a relatively high BET specific surface area of 39.22 m²g⁻¹. With the benefits of the porous structure and the introduction of conductive CNTs, the composite is believed to be advantageous to high ion accessibility, fast ion and electron transport.

More detailed structural information and morphology of Ca₂GeO₁₆ NS/CNT were investigated by TEM. The TEM images of Ca₂GeO₁₆ NS/CNT in Fig. 4a and b confirm that the average thickness of the NS is about 20–40 nm which is consistent with the result of SEM. CNTs with the diameter of about 20–30 nm are distributed on the surface of the Ca₂GeO₁₆ NSs. Fig. 4c shows high-resolution TEM (HRTEM) image of the vertical edge of a Ca₂GeO₁₆ NS perpendicular to basal surface of NSs, which is attributed to folding and curving of NSs (highlighted by the white square line in Fig. 4a). It shows lattice fringes with spacing of 8.01 Å corresponding to the (110) lattice of a Ca₂GeO₁₆ NS. Fig. 4d shows lattice fringes with spacing of 8.01 Å corresponding to the (110) lattice of a Ca₂GeO₁₆ NS.
4.02 Å and 3.59 Å, corresponding to the (111) and (021) lattice planes of a Ca$_2$Ge$_7$O$_{16}$ NS (the area highlighted by the black square line in Fig. 4a), respectively. The SAED pattern (the inset of Fig. 4a) shows the as-prepared Ca$_2$Ge$_7$O$_{16}$ NS is polycrystalline in nature.

Fig. 5a shows the CV curves of Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode, which is used to investigate the lithium insertion–desorption mechanism in the electrode. In the initial sweep, there is a remarkable cathodic peak located around 0.97 V which is ascribed to the decomposition of Ca$_2$Ge$_7$O$_{16}$ into Ca, Ge, Li$_2$O and the formation of the SEI film. Other peaks at 0.69 V and 0.2 V indicate the Li–Ge alloying reactions (Fig. 5a). In the anodic-scan process, a broad peak centered at 0.52 V can be assigned to the delithiation of the Li-metal alloys. Of particular note, three peaks located at 1.05 V, 1.3 V and 2.2 V represent the reoxidation of Ge, corresponding to the conversion reaction. For the subsequent cycles, two main reduction peaks in the range of 0.5 V to 1.0 V and 0 to 0.5 V are observed which correspond to Li–Ge alloying reactions. The reduction peaks in the range of 1.5 V to 1.75 V is corresponding to the reduction of GeO$_2$ to Ge. During the anodic potential sweeps, broad oxidation peaks around 0.5 V are observed, which are associated with the delithiation. The oxidation peaks at 1 V to 2.5 V are associated with the reoxidation of Ge to GeO$_2$. The overall electrochemical reaction process during Li insertion/extraction can be described as follows:

$$\text{Li}^+ + e^- + \text{electrolyte} \rightarrow \text{SEI (Li)}$$

$$\text{Ca}_2\text{Ge}_7\text{O}_{16} + 28\text{e}^- + 28\text{Li}^+ \rightarrow 2\text{CaO} + 7\text{Ge} + 14\text{Li}_2\text{O} (0.97 \text{ V})$$

$$\text{Ge} + x\text{e}^- + x\text{Li}^+ \leftrightarrow \text{Li}_x\text{Ge} (0 \leq x \leq 4.4, 0–0.7 \text{ V})$$

$$\text{Ge} + \text{Li}_2\text{O} \leftrightarrow \text{GeO}_2 + 4\text{Li}^+ + 4\text{e}^- (1–3 \text{ V})$$

Fig. 5b shows the representative galvanostatic charge/discharge profiles of the electrode at a current density of 500 mA g$^{-1}$ after 5 cycles activation at 200 mA h g$^{-1}$ within a cut-off voltage window between 0.01 and 3 V. All the galvanostatic discharge–charge voltage profiles with the consistent voltage platform indicate the stable electrochemical processes as those in the CV measurements (Fig. 5a). The discharge and charge capacities at the 1st, 2nd, 100th, 300th, 500th, 800th, 1000th cycles are 1002.2 and 998.5, 815.4 and 749.7, 626.7 and 612.7, 508.6 and 500, 717.8 and 711.8, 725.5 and 720.8, 652.6 and
**Fig. 3** (a–d) SEM images of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT nanocomposite at various magnifications.

**Fig. 4** (a) Low-resolution TEM image of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT nanocomposite. (b) High-resolution TEM image of the area highlighted by the white circle of (a). (c) and (d) HRTEM images of the Ca$_2$Ge$_7$O$_{16}$ NS. The inset shows the SAED image of (d).
Fig. 5 (a) CV curves and (b) discharge/charge profiles of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode. (c) Cycling performances of different samples at 500 mA g$^{-1}$ after 5 cycles activation at 200 mA g$^{-1}$ between 0.01 and 3 V. (d) CE of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode. (e) Rate performance of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode.
652.1 mA h g\(^{-1}\) at a current density of 500 mA g\(^{-1}\), respectively, as shown in Fig. 5b. The first discharge and charge capacity is 1855.7 and 1263.4 mA h g\(^{-1}\), respectively. Fig. 5c gives the long-term cycling performance of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT at a current rate of 500 mA g\(^{-1}\) after 5 cycles activation at a current rate of 200 mA g\(^{-1}\). Our Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT anode exhibits a superior cycling performance, delivering a high reversible capacity of 724.2 mA h g\(^{-1}\) even after 800 cycles, which is much higher than the previous report.\(^{22}\) After 1000 cycles, the capacity retention is 87% of its 2nd cycle reversible capacity (dropping by only 0.01% per cycle) at 500 mA g\(^{-1}\). The capacity gradually decreases first and then increases (after about 300 cycles), which can be attributed to the reversible formation of a polymeric gel-like layer via electrolyte decomposition, further activation of active materials and the electrocatalytic reversible conversion of some components of SEI films. The phenomenon is usually observed in transition metal oxides anode materials.\(^{31,32}\) Even cycled at a high current density of 1 A g\(^{-1}\) after 500 cycles, the reversible specific capacity of the electrode is still as high as 600.3 mA h g\(^{-1}\), indicating the excellent cycling performance (Fig. S5a and b†). The first CE of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT anodes is 68.1%, which is much higher than the previous reports,\(^{19,21}\) as shown in Fig. 5d. Then, it increases to 98% in the next cycle and reaches a stable value of almost 100% after 10 cycles, indicating a very high reversibility of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT anode. The initial capacity loss is caused by incomplete conversion and the formation of a solid electrolyte interphase (SEI) layer ascribed to the electrolyte decomposition (Fig. S6a,\(^\dagger\) highlighted by the white line).\(^{33}\) After lithiation, the electrode can maintain an integrated structure without pulverization and fracture (Fig. S6b†), resulting in a stable cycle performance. For comparison, the lithium-storage performance of the pristine Ca\(_2\)Ge\(_x\)O\(_{16}\) NS electrode was also studied. The pristine Ca\(_2\)Ge\(_x\)O\(_{16}\) NS electrodes with the thickness about 20–40 nm grow on the Ni foam uniformly (Fig. S7†). By contrast, the capacity (768.75 mA h g\(^{-1}\)) begins to decrease rapidly at 50th cycle, and retains 427.75 mA h g\(^{-1}\) after 200th cycles at 500 mA g\(^{-1}\). After cycling, the pristine Ca\(_2\)Ge\(_x\)O\(_{16}\) NS suffers pulverization and fracture caused by volume variation (Fig. S8†).

To further investigate the electrochemical performance of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT composite, the rate performance was examined. The rate capability of Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT composite in the applied current range of 0.1–5 A g\(^{-1}\) is shown in Fig. 5e. The Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT electrode exhibits charge capacity (reversible capacity) of 1396.3, 919.8, 714.1, 539.1, 342.4, 200 mA h g\(^{-1}\) at rates of 0.1, 0.2, 0.5, 1, 2, 5 A g\(^{-1}\), respectively. As expected, the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT electrode exhibits a better rate performance compared with the NS electrode (Fig. S9†). When the rate returns back to 100 mA g\(^{-1}\) after 100 cycles, the charge capacity can be largely recovered which indicate a good rate performance. A CE is almost 100% for all the cycles except the first cycle due to the formation of a SEI as previously mentioned. After the rate performance test, the coin cell is cycled for additional 100 cycles at 0.1 A g\(^{-1}\), maintaining the capacity of 1001.6 mA h g\(^{-1}\) (99.44% of the sixth cycle reversible capacity), which further confirms the excellent cyclic performance of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT composite anode. The good capability and excellent cycling stability of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT electrode are impressive values when compared to those of many previously reported Ca\(_2\)Ge\(_x\)O\(_{16}\) based electrodes, as shown in Table S1.†

Several contributing factors can be considered for the high specific capacity and excellent cycling stability of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT composite anode. First, the NS structures greatly shorten the ionic diffusion length and provide sufficient electrode–electrolyte contact area for lithium-storage reactions. The presence of the voids between the NS structures will not only relieve the structural alterations caused by the charge–discharge process, thus improving the cycling performance, but also help to store more lithium. Second, the incorporation of CNTs can improve the mechanical strength and increase the electronic contact and conductivity of the anode.\(^{34}\) Last, the nickel foam also plays an important role in enhancing the electrode conductivity by forming a continuous 3D electronic path for fast and stable charge transfer while providing the electrode with a large specific surface area, high porosity, and high mechanical flexibility.

The enhanced ion diffusion and effective electron transfer in the composite electrode are further confirmed by the EIS

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**Fig. 6** (a) Equivalent circuit model of the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT anode. (b) Typical Nyquist plots and fitted EIS plot of the pristine Ca\(_2\)Ge\(_x\)O\(_{16}\) NS and the Ca\(_2\)Ge\(_x\)O\(_{16}\) NS/CNT.
measurements, which were performed in the frequency range between 100 kHz and 10 mHz before the charge and discharge process (Fig. 6). The fitting of EIS data was carried out with a Zview software. The experimental result at the fully discharged state was fitted by a one time-constant equivalent circuit. The data of the Nyquist plots were analyzed by fitting to equivalent electric circuit (EEC), as shown in Fig. 6a. The EIS spectra of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode show the compressed semicircle from the high to medium frequency range of each spectrum, which describes the resistance of SEI and charge transfer (R$_s$) and constant-phase element (CPE1, representing the double-layer capacitance) for the electrodes. A line inclined at approximately 45° at the low frequency, corresponding to the Warburg impedance (W) that is related to the Li$^+$ ions diffusion. On the basis of a simplified equivalent circuit the estimated $R_s$ value of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT (78.4 Ω) is relatively lower than that of the pristine Ca$_2$Ge$_7$O$_{16}$ NSs (118.1 Ω), indicating the improved charge transport properties of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT due to the combination of CNT as a conducting medium. The lithium diffusion coefficient of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT electrode is calculated to be 4.98 $\times$ 10$^{-13}$ cm$^2$ s$^{-1}$, indicating a fast lithium ion diffusion process (Fig. S10†).

By using this Ca$_2$Ge$_7$O$_{16}$ NS/CNT as an additive-free anode and commercial LiCoO$_2$/Al foil as a cathode, we fabricated a coin-type full cell. The electrochemical performance of the anode-limited full cell (that is, when considering the matching of the electrodes, the capacity of the anode is appropriately lower than that of the cathode) was investigated by cycling within the voltage range of 2.0–4.2 V at a current density of 0.2 A g$^{-1}$. After packed, the full cell was subjected to a pre-lithiation cycle by charging and discharging at a low current density. According to a previous report, this procedure should form a solid electrolyte interphase (SEI) layer on the surface of the anode owing to decomposition of the electrolyte. Fig. 7a shows the voltage–capacity profiles of the full cell device for the 1st, 2nd, 10th, 30th, 50th, 80th and 100th charge/discharge cycles with a discharge voltage plateau of about 3.6 V and a charge-voltage plateau of about 3.7 V. The reversible capacities at the 1st, 2nd, 10th, 30th, 50th, 80th and 100th cycles are 1703.7, 1477.1, 1247.8, 1290.7, 1253.6, 1219 and 1197.8 mA h g$^{-1}$, respectively. The binder free full cell exhibits excellent cycle performance with 96% retention of its 10th cycle capacity after 100 cycles (Fig. 7b). To evaluate the potential application of the Ca$_2$Ge$_7$O$_{16}$ NS/CNT electrodes for LIBs, the output voltage of the as-prepared full cell is found to be 4.19 V, which can give a larger current intensity ($\sim$120 mA) to light up 6 commercial blue LEDs, Fig. S11† Thus, it is expected that the Ca$_2$Ge$_7$O$_{16}$ NS/CNT can be utilized as a promising alternative anodic material in LIBs.

Conclusions

In conclusion, a Ca$_2$Ge$_7$O$_{16}$ NS/CNT anode has been fabricated via a simple, fast and high yield hydrothermal method for the first time. The Ca$_2$Ge$_7$O$_{16}$ NS/CNT composites are uniformly grown on the surface of three-dimensional Ni foam. CNTs with the length of about 50–150 nm are well distributed on the surface of the Ca$_2$Ge$_7$O$_{16}$ NSs with the thickness ranging from 20–40 nm. The as-prepared Ca$_2$Ge$_7$O$_{16}$ NS/CNT composites used as the anode of LIBs show excellent cycle performance compared to the pristine Ca$_2$Ge$_7$O$_{16}$ NSs and the reported Ca$_2$Ge$_7$O$_{16}$ based anodes. The outstanding cycling performance is attributed to the unique synergetic effect in the nanoscale between 1D CNTs and Li$^+$ hosting 2D NSs. The designed NS structure with high specific surface area provides sufficient electrode–electrolyte contact area and greatly shortens the ionic diffusion length, while CNTs provide high conductance channels. Therefore, it is expected that such a Ca$_2$Ge$_7$O$_{16}$ NS/CNT nanocomposite is a highly promising anode material for LIBs. Furthermore, the Ca$_2$Ge$_7$O$_{16}$ NS/CNT structure developed here enhance the cycling life can be applicable to other functional nanocomposite materials to improve their cycling stability.

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