



(51) International Patent Classification:

H01M 4/36 (2006.01) *C07K 14/00* (2006.01)
H01M 4/04 (2006.01) *H01M 4/02* (2006.01)
B82Y 40/00 (2011.01) *C01B 25/30* (2006.01)

(21) International Application Number:

PCT/SG2016/050151

(22) International Filing Date:

28 March 2016 (28.03.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10201502440P 27 March 2015 (27.03.2015) SG
 10201507712P 16 September 2015 (16.09.2015) SG

(71) Applicant: **NANYANG TECHNOLOGICAL UNIVERSITY** [SG/SG]; 50 Nanyang Avenue, Singapore 639798 (SG).

(72) Inventors: **FONG, Wenmei Eileen**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **YAN, Qingyu Alex**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **ZHOU, Yanping**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **RUI, Xianhong**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG). **LU, Yan**; c/o Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (SG).

(74) Agents: **KINNAIRD, James Welsh** et al.; Marks & Clerk Singapore LLP, Tanjong Pagar, P.O. Box 636, Singapore 910816 (SG).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

— with sequence listing part of description (Rule 5.2(a))

(54) Title: **BIOCHEMISTRY-DERIVED CARBONACEOUS METALLIC FRAMEWORKS FOR USE IN BATTERIES**

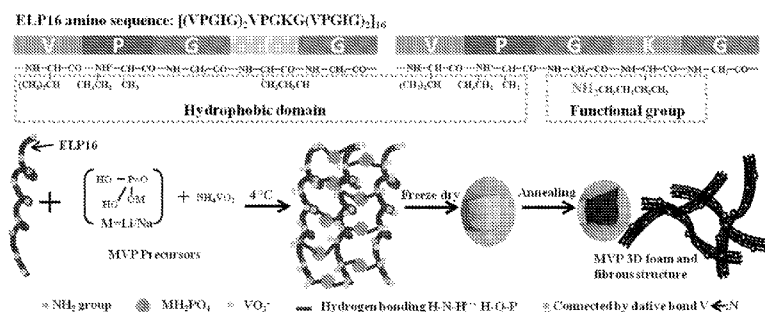


FIG. 1

(57) Abstract: Disclosed herein are materials composed of a porous carbon substrate with a 3D-nanostructure backbone, further containing an active nanomaterial suitable for use in the manufacture of an anode or a cathode. Also disclosed herein are methods of manufacturing said materials, which make use of the agglomeration of a protein/polypeptide to form a 3D-framework throughout which the active material is homogeneously distributed before said protein/polypeptide is carbonised.

BIOCHEMISTRY-DERIVED CARBONACEOUS METALLICS FRAMEWORKS FOR USE IN BATTERIES

Field of Invention

5

This invention relates to composite materials derived from conjugated biochemical materials that may be used in the manufacture of electrodes for batteries. The invention also relates to methods of manufacture of said materials and to electrodes containing said materials.

10 Background

The listing or discussion of an apparently prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

15

The increasing demand for rechargeable batteries in some emerging portable electronic devices, advanced medical devices, and in particular, electric vehicles and hybrid electric vehicles has sparked research efforts in developing lithium ion batteries (LIBs) with high storage capacity and excellent rate performance. Graphite, the most commonly used commercial anode material, encounters some disadvantages such as low theoretical specific capacity (372 mAhg^{-1}) and limited rate capability. Thus, intense efforts have been devoted to searching for new carbon-based anode materials with enhanced Li ion storage capacities. For example, carbon nanotubes, nanofibers, nanobeads, hollow nanospheres, graphene, porous carbon, and their hybrids have been successfully synthesized and investigated in LIBs. Amongst them, nanostructured porous carbon is one of the most promising candidates due to its large surface area and high porosity with unique transport properties. To further improve the Li storage performance of the carbon-based anodes, heteroatoms have also been incorporated within carbon-based anodes. Large number of reports on nitrogen, boron or nitrogen-boron doping in various carbon materials can be found to increase anode performance compared with pure carbon structures. However, the investigation of other light weight elements (such as fluorine, phosphorus and sulfur) doping or co-doping effects on carbon-based anode performance have been relatively unexplored, even though most of them have been found to exhibit excellent performances in other applications, such as oxygen reduction reaction (ORR). It has been reported that fluoride-doping can affect the electronic structure of the carbon materials and create new active sites in the carbon nanostructure.

35

While lithium ion batteries (LIBs) have dominated the market for power sources for portable electronic devices, the high cost of lithium limits the application of LIBs in some emerging areas, such as electronic vehicles (EVs), hybrid electronic vehicles (HEVs), and particularly, large-scale grid energy storage hampers their application. Sodium, also a Group I element, shares similar chemical properties with lithium, and thus is a promising alternative to lithium. More importantly, sodium is much more abundant compared to lithium. As such, sodium ion batteries (SIBs) have gained considerable interest in the past few years.

The development of SIBs is significantly hindered by the unsatisfactory electrochemical performance of electrode materials. Some cathode materials explored for SIBs showed promising performance such as $\text{P2-Na}_{2/3}\text{MnO}_2$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. As the state-of-the-art anode material for LIBs, graphite is nearly electrochemically inactive with sodium due to the large ionic radius of Na^+ . Though many carbonaceous materials with various nanostructures have been investigated as anodes for SIBs, their sodium storage capabilities in terms of specific capacitance or rate capability cannot meet the demands of practical applications. Recently, reports on the potential application of transition metal oxides as anodes for SIBs have emerged. Transition metal oxides such as iron oxides and cobalt oxides possess high theoretical capacities for lithium storage by means of conversion reaction mechanism (e.g., 1005 mA h g^{-1} for Fe_2O_3 , much higher compared to 372 mA h g^{-1} for graphite). Theoretically, such metal oxides are also able to store sodium via similar conversion reaction mechanisms to achieve similar theoretical capacities as lithium storage. However, due to the sluggish sodiation/desodiation reaction kinetics induced by the large ionic radius of Na^+ , the reported metal oxides materials exhibit much inferior capacity for sodium storage compared to that for lithium storage. In order to increase the deliverable capacity for sodium storage, engineering robust nanostructured electrode materials is urgently needed. It is expected that the ion transportation pathway would be significantly decreased and more reactive sites would be created, thereby resulting in fast sodiation/desodiation reactions.

Three-dimensional (3D) hierarchical foam/porous nanoarchitectures have recently attracted significant attention for lithium/sodium energy storage applications by offering sufficient contact area between the electrolyte and electrode, high-rate transportation of ions and electrons, and short solid-state ion diffusion lengths. These properties favor the use of 3D foam/porous nanomaterials in advanced plug-in hybrid vehicles (PHEVs) and electric vehicles (EVs) with rapid charge and discharge requirements. The above properties may be due to the presence of both micro- and meso-pores in the foams. The presence of micro-pores can act as a transport system while the meso-pores provide high surface areas to facilitate high-rate transportation of ions and electrons.

In the field, intensive research effort has been devoted to fabrication of numerous 3D structured battery anodes, such as Cu_6Sn_5 alloy foams, Ni-foam-supported $\text{CoO-Li}_2\text{O}$, Fe_3O_4 /graphene foams and MoS_2 /graphene foams. Hybrid carbon materials containing metallic compounds such as SnO_2 nanocrystals/N-graphene, N-graphene SnO_2 sandwich paper, Fe_3O_4 /N-carbon, $\text{SiO}/\text{N-carbon}$ and so on, have also been reported to have increased anode performances. Current strategies used for the preparation of such 3D foams (or 3D porous carbon scaffolds) include hydrothermal self-assembly, template-assisted preparation, electrostatic spray deposition, chemical vapor deposition (CVD) and atomic layer deposition (ALD). However, syntheses of 3D hybrid carbon architectures is highly challenging, and often requires high energy consumption, e.g., high temperature or high pressure; multi-step reactions; the need for specialized equipment for processes like CVD; or the use of toxic and erosive reagents (such as HF or NaOH). This is particularly so if one wishes to form 3D foam anodes or cathodes, particularly cathode materials with complex stoichiometric compositions.

In addition, much effort has been put into preparing 3D metal oxides architectures, including methods involving post-template oxidation, template-free hydrothermal synthetic route, ethylene glycol-mediated self-assembly process, ionic liquid-assisted synthesis and so on. However, despite this recent progress, assembly of low-dimensional building blocks into 3D hierarchically porous superstructures still remains a challenge.

Biological molecules and organisms (e.g., polysaccharides, proteins, viruses, DNA, peptides, etc.), have been employed to synthesize nanomaterials due to their environmentally friendly synthesis conditions. For example, preparation of hybrid $\text{Au-Co}_3\text{O}_4$ wires synthesized using M13 phage virus for anode materials in lithium ion batteries, biomineralization of uniformly-sized metal phosphate nanoparticles using apoferritin templates, and so on. These can be achieved using recombinant proteins designed to contain tunable structures and motifs to guide the self-assembly of metallic precursors. For example, Au nanowires formed from the self-assembly of gold ions with histidine-rich peptides, metal phosphates nanofibers mineralized by self-assembled hydrophobic peptides, mono-dispersed silver nano-particles grown inside the cavity of a peptide nanoreactor. More importantly, it is possible to genetically engineer molecules to interact with metallic precursors under benign conditions, and to create inorganic nanostructures with high surface areas, with precise control over their compositions, phase, shape and size. For example, peptides, phages, viruses and proteins have been successfully used to guide the formation of FePt , Co_3O_4 and iron oxide nanoparticles (NPs), BaTiO_3 NPs, Co_3O_4 nanowires, FePO_4 nanofibers, and so on. Most of these systems are focused on preparing naturally 0D or 1D nanostructures; construction of

more complex inorganic materials and architectures (e.g., 3D foams) *via* biological routes have not been demonstrated.

Metal vanadium phosphates (MVP), particularly $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) NPs are promising cathode materials for lithium ion batteries and sodium ion batteries due to their excellent thermal stabilities, large reversible capacities, high operating potentials and relatively rapid ionic mobilities. Currently, LVP and NVP are manufactured at the micro or sub-micro scales using traditional energy-intensive solid-state ceramic processes.

Summary of Invention

An object of this invention is to provide a facile strategy for the preparation of LVP and NVP nanostructures supported on hierarchically porous 3D carbon aerogels using recombinant elastin-like polypeptides. Elastin-like polypeptides (ELPs) are known to undergo self-aggregation through a temperature-induced coacervation process, and are widely studied for a wide variety of applications including tissue engineering and bioremediation. Here, we designed and prepared a recombinant protein, ELP16 with amino acid sequence of $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}$, containing repetitive valine, proline, glycine, isoleucine, and lysine amino acid sequences to direct the growth of LVP and NVP particles. Figure 1 illustrates the steps involved in the synthesis. The lysine (K) residues incorporated periodically within the elastin framework provide amine side groups that interact with H_2PO_4^- and VO_3^- ions through hydrogen bonding or/and dative bonding. These interactions serve as 'crosslinks' between two adjacent ELP16 molecules, causing the formation of ELP16 fibers. During annealing, the N atoms combine both phosphates and vanadium, and act as nucleating centers for the formation of LVP or NVP nanoparticles (NPs). Meanwhile, ELP16 is degraded into carbon matter, resulting in carbon-enveloped LVP or NVP NPs dispersed within a 3D conductive carbon aerogel network. The as-synthesized 3D MVP nanostructures show ultrahigh capacity at ultrafast charging/discharging properties and excellent cycle performance as cathodes for Li/Na secondary battery.

A further object of this invention is to provide a way to synthesize 3D hierarchically porous carbon-encapsulated metal oxides *via* the self-assembly of recombinant elastin-like polypeptides containing hexahistidine tag $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}\text{HHHHHH}$ (named ELP16-His). Elastin-like polypeptides (ELPs) consist of repetitive VPGXG sequences, where X is any amino acid except proline (Figure 2). ELPs are known to be soluble in water below their inverse transition temperature (T_i) and aggregate at temperatures above T_i . As such, the physical properties of ELPs make them versatile as tunable 3D scaffolds for tissue

engineering and drug delivery applications. In addition, the hexahistidine (His tag) containing six Histidine amino acids, is known for binding selectively to several metal cations. Here, the ELP domain facilitates the formation of a 3D macroporous scaffold, where metal cations are recruited within the matrix via specific interactions with the His tag. The scaffold is further annealed to yield metal oxides that are uniformly dispersed in a 3D porous carbon matrix. The synthesis route of the 3D hierarchically porous carbon-encapsulated metal oxides is shown in Figure 2.

A further object of this invention is to provide a bio-inspired approach to synthesize three-dimensional, porous graphitized carbon foams containing metal fluoride nanoparticles. In particular, recombinant elastin-like polypeptides (ELPs) containing FLAG tags [(VPGIG)₂VPGKG(VPGIG)₂]₁₆CDYKDDDDKL (named ELK16-FLAG) were prepared (Figure 3). An exemplified recombinant ELP16-FLAG protein is depicted in SEQ ID NO: 3. ELP is an interesting class of polypeptides based on the repetitive pentapeptide motif Val-Pro-Gly-Xaa-Gly (where the "guest residue" Xaa is any amino acid except Pro), which is known to undergo self-aggregation through a temperature induced process and are widely studied for a wide variety of applications including tissue engineering and bioremediation. The FLAG tag (CDYKDDDDKL) was included at the C-terminus of the protein as a purification tag as well as to serve as a carboxyl-rich site to facilitate binding of metallic ions.

The ELK16-FLAG proteins were chemically crosslinked via the lysine residues (K) incorporated periodically throughout the elastin backbone. Addition of a non-toxic crosslinker bis(sulfosuccinimidyl)suberate (BS3) yielded insoluble three-dimensional foams, which could be subsequently immersed into solutions containing metal fluoride precursors (i.e., ionic liquid (BmimBF₄) and MnCl₂·4H₂O). The mixture was subsequently annealed at 600 °C in Ar atmosphere to obtain the final 3D graphitized carbon foam containing MnF₂ nanocrystallites (Figure 3).

Aspects and embodiments of the invention are set out in detail in Claims 1 to 48 below.

Drawings

Figure 1 is a schematic illustrating the mechanisms in the synthesis of MVP 3D foams using recombinant ELP16 proteins.

Figure 2 is a scheme illustrating the synthesis of carbon-encapsulated metal oxides using recombinant elastin-like polypeptides (ELP16-His). The single letter amino acid sequence of ELP16-His is shown.

Figure 3 (a) shows the amino acid sequence of ELK16-FLAG. (b) Schematic illustrating the synthesis of N,F co-doped 3D porous carbon scaffold supported MnF_2 nanocrystals with assistance of crosslinked ELK16-FLAG proteins.

Figure 4 is an XRD spectra of as-synthesized (A) LVP and (B) NVP.

5 Figure 5: (A – C) are FESEM images of as-synthesized LVP 3D foams at various magnifications; (D) is a TEM image showing LVP nanoparticles embedded within a carbon matrix; (E) is the measured lattice spacing (0.367 nm) corresponding to (211) plane of LVP. (F – H) are FESEM images of as-synthesized NVP 3D foams at various magnifications; (I) is a TEM image confirming NVP nanoparticles embedded within a carbon matrix; (J) is the
10 measured lattice spacing (0.442 nm) corresponding to (104) plane of NVP.

Figure 6 provides: TEM images of as-synthesized LVP@C/CAs (A – B); and NVP@C/CAs (C – D) at low magnifications, confirming the inter-connected fibrous structures.

Figure 7 depicts nitrogen adsorption and desorption isotherms at 77 K for (A) as-synthesized LVP@C/CAs and (B) as-synthesized NVP@C/CAs, with inserts showing pore size
15 distributions.

Figure 8 contains: FESEM images of (A) ELP16, LiH_2PO_4 and NH_4VO_3 , (B) ELP16 and LiH_2PO_4 , and (C) ELP16 and NH_4VO_3 mixtures obtained after freeze drying; (D) FTIR spectra of LVP precursors only (curve a), ELP16 + LVP precursors (curve b), and ELP16 only (curve c). The shifts in P-O stretching, V-O-V stretching, and C-NH₂ stretching peaks
20 are indicated.

Figure 9 contains: (A) FESEM image of 7.5% ELP solution after freeze drying; (B) FESEM image of ELP16+ LVP precursor solution put at room temperature for 1 h, followed by freeze drying. In both instances, no fibrous structures were observed.

Figure 10 contains images depicting: initial charge-discharge voltage profiles of (A) LVP and
25 (B) NVP cathodes at 1C. Insets show the corresponding cycling performances for each material; Galvanostatic discharging profiles of (C) LVP and (D) NVP cathodes at current rates of 5C to 200C (their discharge capacities versus C rates are summarized in the insets). (E) Cycling stability of LVP and NVP at 100C. (F) Ragone plots of our 3D MVP cathodes, compared with some advanced active materials of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (up triangles), CNT/ FePO_4 nanowires (down triangles), LiFePO_4/C (diamonds), LVP/C thin film (right triangles),
30 $\text{Na}_3\text{Ni}_2\text{SbO}_6$ (hexagons), NVP/graphene (stars).

Figure 11 depicts the charge/discharge performance of (a) LVP||Li at 0.1 C from 0 to 4.3 V; (b) LTO||Li at 0.1 and 1C from 1 to 3 V.

Figure 12 depicts the charge/discharge performance of LVP||LTO full cell at 0.1C from 1.3 to
35 3.3V.

Figure 13 depicts FESEM images of crosslinked ELP16-His (a) before and (b) after treatment with Fe^{3+} .

Figure 14 depicts XRD spectra of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ (a) and $\text{Co}_3\text{O}_4@\text{C}$ (b).

Figure 15 depicts a high-resolution X-ray photoelectron spectroscopy spectrum of Fe 2p for $\text{Fe}_3\text{O}_4@\text{C}$.

Figure 16 depicts: (a - b) FESEM images of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ at different magnifications; (c - d) TEM images of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.

Figure 17 depicts the thermal gravity analysis of as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ and $\text{Co}_3\text{O}_4@\text{C}$.

Figure 18 depicts nitrogen adsorption and desorption isotherms at 77 K for as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ (a) and $\text{Co}_3\text{O}_4@\text{C}$ (b).

Figure 19 depicts (a) FESEM image of as-synthesized $\text{Co}_3\text{O}_4@\text{C}$; (b - c) TEM images of as-synthesized $\text{Co}_3\text{O}_4@\text{C}$, showing nanoparticles of around 5 nm embedded in a carbon matrix.

Figure 20 depicts: (a) CV curves of a fresh SIB with $\text{Fe}_3\text{O}_4@\text{C}$ electrode at a scan rate of 0.1 mV s^{-1} within a potential range of 0.001 to 3.0 V (vs. Na/Na^+); (b) the 1st charge-discharge profiles of the cells with $\text{Fe}_3\text{O}_4@\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes at a current density of 0.1 A g^{-1} ; (c) rate capabilities of the cells with $\text{Fe}_3\text{O}_4@\text{C}$, bare Fe_3O_4 , and Fe_2O_3 electrodes; (d) cycling performance of cell with the $\text{Fe}_3\text{O}_4@\text{C}$ electrode at 0.1 A g^{-1} ; (e) cycling performance of the cell with $\text{Fe}_3\text{O}_4@\text{C}$ electrode at 0.2 and 0.5 A g^{-1} .

Figure 21 depicts CV curves of a fresh SIB with $\text{Fe}_3\text{O}_4@\text{C}$ electrode at different scan rates within a potential range of 0.001 to 3.0 V (vs. Na/Na^+).

Figure 22 depicts: (a) rate capability of the cell with $\text{Co}_3\text{O}_4@\text{C}$ electrode. Inset shows the 1st charge-discharge profile of the cell at 0.1 A g^{-1} ; (b) cycling performance of the cell with $\text{Co}_3\text{O}_4@\text{C}$ electrode at 0.5 A g^{-1} .

Figure 23 depicts: (a - c) SEM and (d - f) TEM images of $\text{MnF}_2@\text{N,F-C}$, showing the porous structures of the as-annealed ELK16-FLAG hydrogel scaffolds containing MnF_2 nanocrystals. Inset in (f) shows the FFT image of the area enclosed by the red square in (f).

Figure 24 depicts: (a) XRD patterns of $\text{MnF}_2@\text{N,F-C}$ and annealed ELK16-FLAG hydrogel scaffold; (b) Raman spectra for $\text{MnF}_2@\text{N,F-C}$ and N,F-C scaffold; (c) nitrogen adsorption-desorption isotherms and pore size distribution curve (inset) for $\text{MnF}_2@\text{N,F-C}$, N,F co-doped carbon scaffold and N doped carbon scaffold; XPS spectra of (d) C1s, (e) N1s and (f) F1s of $\text{MnF}_2@\text{N,F-C}$.

Figure 25 depicts TGA curves of $\text{MnF}_2@\text{N,F-C}$, ELK16-FLAG hydrogel in N_2 and ELK16-FLAG hydrogel in air.

Figure 26 depicts the XPS spectrums of O1s in $\text{MnF}_2@\text{N,F-C}$.

Figure 27 depicts: SEM images of crosslinked ELK16-FLAG scaffolds (a) before and (b) after treatment with ionic liquid IL (4h), Mn^{2+} (4h) and IL (overnight). Insets in (a) and (b)

show the appearance of the hydrogels in each instance. SEM images of crosslinked ELK16-FLAG hydrogel after treatment with Mn^{2+} (4h)/IL (4h) / Mn^{2+} (overnight) before (c) and after annealing (d) at 600°C for 4h in Argon atmosphere.

Figure 28 depicts (a-b) SEM images and (c) XRD patterns of the sample prepared using crosslinked ELK16 control as the starting scaffold. (d-e) TEM images of the annealed sample showing a dense crystallized carbon matrix, where MnF_2 crystallites were clearly absent. Lattice spacings measured in (e) correspond to that of graphitized carbon.

Figure 29 depicts electrochemical characteristics of the $\text{MnF}_2@\text{N,F-C}$ anode: a) The first four galvanostatic charge/discharge curves and cycling performance for $\text{MnF}_2@\text{N,F-C}$ anode; b) cycling performance at a rate of 0.1 C for $\text{MnF}_2@\text{N,F-C}$ anode, N,F co-doped carbon scaffold and N doped carbon scaffold; c) rate performance at different rates for $\text{MnF}_2@\text{N,F-C}$ anode, N,F co-doped carbon scaffold and N doped carbon scaffold; d) cycling performance at a rate of 10 C for $\text{MnF}_2@\text{N,F-C}$ anode

Figure 30 depicts TEM images of the discharged $\text{MnF}_2@\text{N,F-C}$ anode after 2000 cycles at a rate of 10 C.

Description

As mentioned hereinbefore, an object of this invention is to provide a facile strategy for the preparation of MVP nanostructures supported on hierarchically porous 3D carbon aerogels using recombinant elastin-like polypeptides. The as-synthesized 3D MVP nanostructures show ultrahigh capacity at ultrafast charging/discharging properties and excellent cycle performance as cathodes for Li/Na secondary battery.

Thus, according to a first aspect of the invention, there is provided a composite material comprising:

- a nanofibrous carbon matrix substrate;
- a nanocrystalline mixed-metal phosphate distributed throughout the nanofibrous carbon matrix substrate; and

- an amorphous carbon coating on the nanocrystalline mixed-metal phosphate, wherein:

- the amorphous carbon coating on the mixed-metal phosphate is from 1 nm to 10 nm thick, optionally from 2 nm to 7 nm, such as 5 nm;

- the total carbon content of the composite material is from 1 wt% to 30 wt%, optionally from 5 wt% to 25 wt%, such as from 18 wt% to 22 wt%; and

- the nanocrystalline mixed-metal phosphate has a diameter of from 100 to 300 nm and has a chemical composition according to formula I:



where:

x and z are independently 1 or 3; y is 1 or 2; A is Na or Li; and M is selected from V, Fe, Ni, Mn and Co,

provided that:

when M is selected from Fe, Ni, Mn and Co, then x, y and z are 1; and

when M is V, then x and z are 3, and y is 2.

It will be understood that the terms "includes," "including," "comprises," and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Accordingly, the terms "includes," "including," "comprises," and/or "comprising," encompasses the more restrictive terms "consisting essentially of" and "consisting of" and the former terms may be replaced by either of the latter terms in all aspects or embodiments herein.

When used herein the term "nanofibrous carbon matrix substrate" refers to a porous network constructed from a plurality of interconnected/fused nanofibres. When used herein, the term "nanofiber" refers to a fibre having a diameter of less than 2000 nm.

The nanofibrous carbon matrix substrate may have any suitable porosity that enables the invention described herein to work. For example, in the first aspect of the invention, the porous, nanofibrous carbon matrix substrate may have a BET surface area of from $75 \text{ m}^2 \text{ g}^{-1}$ to $175 \text{ m}^2 \text{ g}^{-1}$. The porous nature of the nanofibrous carbon matrix substrate of the first aspect of the invention may be due to the presence of mesopores and/or macropores. The macropores may be between fibres, while the mesopores may be a pore within a component fibre of the carbon matrix. Unless otherwise stated, when used herein "mesopores" are pores having a diameter of from 2 nm to 50 nm and "macropores" are pores having a diameter of greater than 50 nm.

In certain embodiments of the invention that may be mentioned herein, the nanofibrous carbon matrix substrate may comprise both mesopores and macropores. For example:

(a) the mesopores may have a diameter of from 1 nm to 20 nm (e.g. from 2 nm to 10 nm, such as from 3 nm to 8 nm); and/or

(b) the macropores may have a diameter of from 50 nm to 10 μm (e.g. from 1 μm to 5 μm , such as from 2 μm to 4 μm). In alternative or additional embodiments that may be mentioned herein, the mesopores in the carbon matrix may have a pore size distribution centered at from 1 nm to 10 nm, optionally from 2 nm to 5 nm, such as from 3 nm to 4 nm, as measured using BET surface area analysis.

The term “nanocrystalline” when used herein refers to a particle having a size of less than 1000 nm in diameter that is substantially crystalline (e.g. >70% by volume, such as > 90% by volume, such as fully crystalline) in nature when examined using X-ray powder diffraction or other suitable analytical techniques.

The nanocrystalline mixed-metal phosphate of the above-mentioned aspect may be any that falls within the scope of Formula I and its provisos. Particular nanocrystalline mixed-metal phosphates of formula I that may be mentioned herein include $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ or $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

When used herein “distributed throughout” refers to the distribution of a material within a matrix substrate, where the material may be partially embedded into the matrix substrate or entirely embedded within the substrate. In particular embodiments of the invention that may be mentioned herein, the nanocrystalline mixed-metal phosphate may be homogeneously distributed throughout the carbon matrix substrate

In a second aspect of the invention, there is provided a method of preparing a composite material according to the first aspect of the invention and its embodiments, wherein the process comprises the steps of:

(a) providing an aqueous solution containing an elastin-like polypeptide that comprises lysine residues;

(b) adding one or more aqueous solutions containing mixed-metal phosphate precursor compounds to the solution containing the elastin-like polypeptide to form a conjugate mixture;

(c) freezing the conjugate mixture and lyophilizing it to provide a lyophilized conjugate; and

(d) annealing the lyophilized conjugate to provide a composite material according to the first aspect of the invention and any of its embodiments.

When used herein the phrase “according to the n^{th} aspect of the invention and its embodiments” (“ n^{th} ” referring to the numbered aspect of the invention) means that the aspect referred to and any of its embodiments (or technically sensible combinations thereof) are

encompassed. Therefore, when the phrase “according to the first aspect of the invention and its embodiments” is used directly above, it is intended to mean that the second aspect of the invention relates to a method for making a composite material according to the first aspect of the invention or any of its embodiments and any technically sensible combination of said embodiments.

Any elastin-like polypeptide that comprises lysine residues may be used herein. Examples of such peptides include, but are not limited to $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}$ and functional equivalents thereof. An example of an equivalent is depicted in SEQ ID NO: 1 which happens to vary in sequence due to a cloning strategy exemplified herein. Without wishing to be bound by theory, it is believed that multiple lysine residues may be responsible for binding the MVPs in place and the regular distribution of lysines in the peptide $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}$ results in a homogeneous distribution of MVP nanocrystals in the final product following annealing.

The mixed metal phosphate precursors may be any suitable precursors that can be used to make a mixed metal phosphate according to Formula I. For example, when:

- (a) the mixed-metal phosphate is $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the mixed-metal phosphate precursors may be NH_4VO_3 and LiH_2PO_4 (e.g. prior to step (b) being conducted, an aqueous precursor solution containing NH_4VO_3 is prepared having a concentration of 0.2 M and a separate aqueous precursor solution containing LiH_2PO_4 is prepared having a concentration of 0.3 M);
- (b) the mixed-metal phosphate is $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, the mixed-metal phosphate precursors may be NH_4VO_3 and NaH_2PO_4 (e.g. prior to step (b) being conducted, an aqueous precursor solution containing NH_4VO_3 is prepared having a concentration of 0.2 M and a separate aqueous precursor solution containing NaH_2PO_4 is prepared having a concentration of 0.3 M);
- (c) the mixed-metal phosphate is $\text{NaFe}(\text{PO}_4)$, the mixed-metal phosphate precursors may be Na_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$; or NaNO_3 , $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$; or Na_3PO_4 and FeCl_3 .

In step (b) of the second aspect of the invention, the concentration of the elastin-like polypeptide in the resulting conjugate mixture may be from 2.5% wt/vol to 20% wt/vol, optionally from 5% wt/vol to 10% wt/vol, such as 7.5% wt/vol. In addition, in step (b) of the second aspect of the invention, when:

- (a) the mixed-metal phosphate is $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and the mixed metal precursors are NH_4VO_3 and LiH_2PO_4 , then the concentration of NH_4VO_3 in the conjugate mixture may be

from 100 mM to 150 mM, such as 125 mM and the concentration of LiH_2PO_4 in the conjugate mixture may be from 175 mM to 200 mM, such as 187.5 mM;

(b) the mixed-metal phosphate is $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and the mixed metal precursors are NH_4VO_3 and NaH_2PO_4 , then the concentration of NH_4VO_3 in the conjugate mixture may be from 100 mM to 150 mM, such as 125 mM and the concentration of NaH_2PO_4 in the conjugate mixture may be from 175 mM to 200 mM, such as 187.5 mM.

In step (c) of the second aspect of the invention, the lyophilization may be conducted by freeze-drying. In step (d) of the second aspect of the invention, the annealing may be conducted at a temperature of from 700°C to 900°C for from 1 hour to 24 hours, optionally at a temperature of from 750°C to 800°C for from 5 hours to 15 hours.

In a third aspect of the invention, there is provided a cathode comprising a composite material according to the first aspect of the invention and its embodiments. The composite material may comprise from 70 to 85 wt% of the cathode. The cathode may have one or more of the following properties:

- (a) a potential hysteresis of less than 0.06 V;
- (b) an initial discharge capacity of from 90 to 150 mA h g^{-1} at 1C;
- (c) a coulombic efficiency of from 95 to 99.5%;
- (d) a capacity retention of from 98.0 to 99.9% during 100 charge/discharge cycles at 1C;
- (e) a discharge capacity of from 50 to 80 mA h g^{-1} at 100C; and
- (f) a capacity retention of from 98.0 to 99.5% during 1000 charge/discharge cycles at 100C.

As mentioned hereinbefore, a further object of this invention is to provide a way to synthesize 3D hierarchically porous carbon-encapsulated metal oxides via the self-assembly of recombinant elastin-like polypeptides containing hexahistidine tag $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}\text{HHHHHH}$ (named ELP16-His). An exemplified recombinant ELP16-His protein is depicted in SEQ ID NO: 2 herein. The resulting scaffold may have particularly good properties as discussed hereinbelow (e.g. see the examples for a discussion of particular advantages that may be mentioned herein).

Thus, in a fourth aspect of the invention, there is provided a composite material comprising:

- a nanofibrous carbon matrix substrate; and
- nanoparticles of a metal oxide encapsulated within the nanofibrous carbon matrix substrate,

wherein:

the nanofibrous porous network structure has a BET surface area of from 20 $\text{m}^2 \text{g}^{-1}$ to 40 $\text{m}^2 \text{g}^{-1}$;

the total carbon content of the composite material is from 1 wt% to 30 wt%, optionally from 5 wt% to 29 wt%, such as from 22 wt% to 28 wt%;

the metal oxide has a diameter of from 1 nm to 15 nm and is selected from the group consisting of Fe_3O_4 , Fe_2O_3 , CoO , Co_3O_4 , NiO , MnO_2 , MnO , and Mn_2O_3 .

10 In the fourth aspect of the invention, the nanofibrous carbon matrix may have a BET surface area of from 25 $\text{m}^2 \text{g}^{-1}$ to 32 $\text{m}^2 \text{g}^{-1}$, optionally from 28 $\text{m}^2 \text{g}^{-1}$ to 30 $\text{m}^2 \text{g}^{-1}$. The porous nature of the nanofibrous carbon matrix substrate of the second aspect of the invention may be due to the presence of macropores. The macropores may be between fibres that comprise the carbon matrix. For example, the macropores within the carbon matrix may have a diameter
15 of from 50 nm to 10 μm , optionally from 1 μm to 5 μm , such as from 2 μm to 4 μm .

When used herein “nanoparticles” may refer to a material that is crystalline or amorphous. For example, in embodiments of the invention that may be mentioned herein, the term “nanoparticles” may refer to a material that is substantially amorphous, such as greater than
20 50% amorphous, such as greater than 75% amorphous, for example greater than 95% amorphous as measured using powder X-ray diffraction or any other suitable method of measurement of this property.

25 In certain embodiments of the fourth aspect of the invention, the carbon matrix may be composed of interconnected carbon microspheres having a diameter of from 2 μm to 10 μm , optionally from 4 μm to 8 μm , such as around 6 μm . In yet further embodiments of the fourth aspect of the invention, the nanoparticles may be homogeneously distributed throughout the carbon matrix. For example, the particles may be partially embedded within the surface of the nanofibres or fully encapsulated within the nanofibres.

30

In certain embodiments of the fourth aspect of the invention that may be mentioned herein, the nanoparticles of the metal oxide may have a size of from 1 nm to 10 nm, optionally from 2 nm to 7 nm, such as 5 nm. Particular metal oxides that may be mentioned herein are Fe_3O_4 and Co_3O_4 .

35

In a fifth aspect of the invention, there is provided a method of preparing a composite material according to the fourth aspect of the invention and its embodiments, wherein the process comprises the steps of:

- (a) reacting an elastin-like polypeptide that comprises lysine residues and a metal conjugating group with a protein crosslinking agent and lyophilizing the resultant product to provide a lyophilised, cross-linked scaffold;
- (b) rinsing the lyophilised, cross-linked scaffold with a metal oxide precursor solution to provide a first conjugate;
- (c) washing the conjugate with water to form a washed conjugate;
- (d) freezing the washed conjugate and lyophilizing it to provide a lyophilized conjugate; and
- (e) annealing the lyophilized conjugate to provide a composite material according to the fourth aspect of the invention and its embodiments.

Any elastin-like polypeptide that comprises lysine residues and a metal conjugating group may be used herein. Examples of such peptides include, but are not limited to $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}\text{CDYKDDDDKL}$ and $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}\text{HHHHHH}$. Without wishing to be bound by theory, it is believed that the multiple lysine residues may help to form an agglomerated mass of protein when a suitable protein crosslinking agent is added (e.g. (bis)sulfosuccinimidyl suberate), such that the metal conjugating groups (e.g. the sequence HHHHHH of $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}\text{HHHHHH}$) are homogeneously distributed throughout the agglomerated protein, subsequently resulting in a homogeneous distribution of metal oxide throughout the annealed carbon matrix.

When used herein “protein crosslinking agent” refers to any suitable agent that can form a covalent bond between a first protein and a second protein. It will be understood that the terms “first protein” and “second protein” may refer to parts of the same protein chain that are suitably far apart for a crosslinking to occur. In proteins containing multiple lysine groups, a suitable protein crosslinking agent that may be mentioned herein is (bis)sulfosuccinimidyl suberate.

When used herein, the term “metal conjugating group” may refer to any moiety attached to a protein that can conjugate a metal and/or a metal oxide to the protein. Examples of suitable conjugating groups include, but are not limited to sequences comprising negatively-charged amino acids at physiological pH glutamic acid (E) and aspartic acid (D) or histidine. These sequences may be of a single kind of amino acid, such as HHHHHH, EEEEE, DDDD or any suitable combination of said amino acids, such as HGHDEH, DDDEEE, EEGGHDD and

the like. Additionally or alternatively, the metal conjugating group may also comprise other amino acid groups, whether positively charged or neutral, with examples including, but not limited to conjugating groups such as CDYKDDDDKL, KKKKRRRR, LDLDDHHKL and the like. Particular metal conjugating groups that may be mentioned herein may contain multiple
5 histidine residues, as described above for the protein [(VPGIG)₂VPGKG(VPGIG)₂]₁₆HHHHHH or containing a core of negatively charged residues, such as CDYKDDDDKL as used hereinbelow.

In step (a) of the fifth aspect of the invention:

- 10 (i) the molar ratio of the reactive group in the crosslinking agent to the lysine amino groups in the elastin-like polypeptide that comprises lysine residues and a metal conjugating group may be from 1:1 to 10:1, such as 1.5:1; and/or
- (ii) the concentration of the elastin-like polypeptide is from 5% wt/vol to 20% wt/vol, optionally from 7.5% wt/vol to 12.5% wt/vol, such as 10% wt/vol; and/or
- 15 (iii) the lyophilization step may be conducted by freeze-drying.

In step (b) of the fifth aspect of the invention, the lyophilized scaffold is rinsed with a metal oxide precursor solution. By "rinsing", it is meant that the scaffold is contacted temporarily with an amount of the metal oxide precursor solution for a suitable period of time (e.g. the
20 rinsing may be conducted for from 10-20 minutes or overnight). Any suitable metal oxide precursors that can provide Fe₃O₄, Fe₂O₃, CoO, Co₃O₄, NiO, MnO₂, MnO, and Mn₂O₃ may be used. For example, when:

- (i) the metal oxide is Fe₃O₄, the metal oxide precursor may be a solution of Fe(NO₃)₃ in a monohydric alcohol (e.g. methanol or ethanol); and
- 25 (ii) the metal oxide is Co₃O₄, the metal oxide precursor may be a solution of Co(NO₃)₂ in a monohydric alcohol (e.g. methanol or ethanol).

In step (c) of the fifth aspect of the invention, the washing step involved contacting the first conjugate with water for a suitable period of time to remove any unbound materials from step
30 (b). In step (d) of the fifth aspect of the invention, the lyophilization step may be conducted by freeze-drying. In step (e) of the fifth aspect of the invention, the annealing may be conducted at a temperature of from 250°C to 400°C for from 15 minutes to 10 hours, optionally at a temperature of from 275°C to 325°C for from 30 minutes to 1 hour.

- 35 In a sixth aspect of the invention, there is provided an anode comprising a composite material according to the fourth aspect of the invention and its embodiments. In certain embodiments of the invention, the composite material may comprise from 70 to 85 wt% of

said anode. In yet further embodiments of the invention that may be mentioned herein, the anode may have one or more of the following properties:

- (a) an initial discharge capacity of from 1000 to 1500 mA h g⁻¹ at 1 A g⁻¹;
- (b) an initial charge capacity of from 500 to 700 mA h g⁻¹ at 1 A g⁻¹; and
- (c) An initial columbic efficiency of from 40 to 50%.

In yet a further object of this invention, it is desired to provide a bio-inspired approach to synthesize three-dimensional, porous graphitized carbon foams containing metal fluoride nanoparticles with improved properties. Thus, in a seventh aspect of the invention, there is provided a composite material comprising:

a N- and F-doped porous carbon matrix substrate; and
a nanocrystalline metal fluoride distributed throughout the porous carbon matrix substrate, wherein:

the metal fluoride is MnF₂;

the N:C weight ratio in the carbon matrix substrate is from 1:20 to 1:5, optionally from 1:10 to 1:6.67, such as from 1:9.09 to 1:8.33, as determined by X-ray photoelectron spectroscopy; and

the ratio of doped F to metal fluoride F is from 1:1 to 1:2, such as 1:1.3, as determined by X-ray photoelectron spectroscopy.

In embodiments of the seventh aspect of the invention, the porous carbon substrate may have a BET surface area of from 80 m² g⁻¹ to 110 m² g⁻¹, such as from 90 m² g⁻¹ to 95 m² g⁻¹. The porous nature of the nanofibrous carbon matrix substrate of the seventh aspect of the invention may be due to the presence of macropores and mesopores. For example:

(i) the macropores within the carbon matrix may have a diameter of from 400 to 600 nm, such as around 500 nm; and/or

(ii) the mesopores may have a diameter of from 1 nm to 100 nm, optionally from 2 nm to 60 nm, such as from 3 nm to 50 nm, such as from 4 nm to 25 nm.

In additional or alternative embodiments, the mesopores may have a first pore size distribution centered at from 1 nm to 10 nm, optionally from 2 nm to 5 nm, such as from 3 nm to 4 nm, and a second pore size distribution centered at from 15 nm to 35 nm, optionally from 20 nm to 30 nm, such as from 24 nm to 26 nm.

In yet further embodiments of the seventh aspect of the invention, the intensity of disordered carbon: intensity of graphene carbon as measured using Raman spectroscopy may be from 1:0.8 to 1:1, optionally from 1:0.90 to 1:0.95, such as 1:0.93.

In an eighth aspect of the invention, there is provided a method of preparing a composite material according to the seventh aspect of the invention and its embodiments, wherein the process comprises the following ordered steps of:

- 5 (a) reacting an elastin-like polypeptide that comprises lysine residues and a metal conjugating group with a protein crosslinking agent and lyophilizing the resultant product to provide a lyophilised, cross-linked scaffold;
- (b) immersing the lyophilised cross-linked scaffold in a solution comprising an ionic fluoride source to provide a first conjugate;
- 10 (c) immersing the first conjugate in a solution comprising a water-soluble metal salt (e.g. a metal chloride) to provide a second conjugate;
- (d) optionally freezing the second conjugate and lyophilizing it to provide a lyophilized conjugate; and
- (e) annealing the second conjugate or lyophilized conjugate to provide a
15 composite material according to the seventh aspect of the invention and its embodiments.

Any elastin-like polypeptide that comprises lysine residues and a metal conjugating group may be used herein. Examples of such peptides include, but are not limited to those mentioned hereinbefore and [(VPGIG)₂VPGKG(VPGIG)₂]₁₆CDYKDDDDKL. Without wishing
20 to be bound by theory, it is believed that the multiple lysine residues may help to form an agglomerated mass of protein when a suitable protein crosslinking agent is added (e.g. (bis)sulfosuccinimidyl suberate), such that the metal conjugating groups (e.g. the sequence CDYKDDDDKL of [(VPGIG)₂VPGKG(VPGIG)₂]₁₆CDYKDDDDKL) are homogeneously distributed throughout the agglomerated protein, subsequently resulting in a homogeneous
25 distribution of metal fluoride throughout the annealed carbon matrix.

In step (a) of the eighth aspect of the invention:

- (i) the molar ratio of the reactive group in the crosslinking agent to the lysine amino groups in the elastin-like polypeptide that comprises lysine residues and a metal
30 conjugating group is from 1:1 to 10:1, such as 2.68:1; and/or
- (ii) the lyophilization step may be conducted by freeze-drying.

In step (b) of the eighth aspect of the invention, the ionic fluoride source may be BmimBF₄; and/or in step (c), the metal chloride may be MnCl₂. In step (d) of the eighth aspect of the invention (when present), the lyophilization step may be conducted by freeze-drying. In step
35 (e) of the eighth aspect of the invention, the annealing is conducted at a temperature of from

480°C to 700°C for from 1 hour to 10 hours, optionally at a temperature of from 575°C to 625°C for from 3 hours to 5 hours.

In a ninth aspect of the invention, there is provided an anode comprising a composite material according to the seventh aspect of the invention and its embodiments. In certain embodiments of the invention, the composite material may comprise from 85 to 95 wt% of the anode.

It is of particular note that all of the materials disclosed herein are 3D nanomaterials, rather than 0D, 1D or 2D nanomaterials (i.e. the nanofibrous carbon matrix substrate and/or the N- and F-doped porous carbon matrix substrate described herein are 3D-nanomaterials). It will be understood by those skilled in the art that the nanofibrous carbon matrix substrate and/or the N- and F-doped porous carbon matrix substrate described herein may also be described either as a hydrogel or an aerogel that consist of three dimensional (3D) nanostructural solid networks, depending on the infilling medium in the interspaces, that is, water and air, respectively.

The aspects and embodiments of the invention may show one or more of the following advantages. The compositions provided herein may provide improved materials with an improved specific capacitance, rate capability and rate transportation of ions, amongst other things. The method of preparation disclosed herein may provide advantages in ease of preparation of such materials and enable the formation of 3D-carbonaceous scaffolds that enable the homogeneous distribution of materials suitable for use in a cathode or anode (e.g. as the active material composition). The 3D nanomaterials described herein may also provide higher energy and charge densities due to their large surface areas in contact with the electrolyte (and hence, large Li^+ source). This in turn may lead to much better electrochemical properties when evaluated as anodes/cathodes.

Examples

Example 1 - Formation of LVP/NVP Cathode Materials and Characterisation Thereof

Metal vanadium phosphates (MVP), particularly $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP), are regarded as the next-generation cathode materials in lithium/sodium ion batteries. These materials possess desirable properties such as high stability, theoretical capacity and operating voltages. Yet, low electrical/ionic conductivities of LVP and NVP have limited their applications in demanding devices such as electric vehicles (EVs). In this work, a novel

synthesis route for the preparation of LVP/NVP micro/meso-porous 3D foams *via* assembly of elastin-like polypeptides is demonstrated. The as-synthesized MVP 3D foams consist of micro-porous networks of meso-porous nanofibers, where the surfaces of individual fibers are covered with MVP nanocrystallites. TEM images further reveal that LVP/NVP nanoparticles are about 100 – 200 nm in diameter – each particle enveloped by a 5 nm thick carbon shell. The MVP 3D foams prepared in this work exhibit ultrafast rate capabilities (79 mA h g⁻¹ at 100C and 66 mA h g⁻¹ at 200C for LVP 3D foams; 73 mA h g⁻¹ at 100C and 51 mA h g⁻¹ at 200C for NVP 3D foams) and excellent cycle performance (almost 100% performance retention after 1000 cycles at 100C); their properties are far superior compared to current state-of-the-art active materials.

Materials Characterization

Powder X-ray diffraction (XRD, Shimadzu Powder) was performed using Cu K α radiation to identify the crystalline phases of the synthesized materials. The morphologies and particle sizes were determined by analyzing images acquired by field-emission scanning electron microscope (FESEM) and transmission electron microscope (TEM). FESEM images were taken using JEOL Model JSM-7600F. TEM images were acquired using JEOL 2010F TEM operated at an accelerating voltage of 200 kV. FT-IR spectra were recorded on a Fourier transform infrared spectrometer (Perkin-Elmer) with a DGTS detector. Nitrogen adsorption/desorption isotherms were conducted at 77 K (ASAP 2020).

Expression and purification of ELP16

The plasmid pET22b containing the gene encoding for ELP16 was constructed by modifying a previously reported construct (Tjin, M. S.; Chua, A. W. C.; Ma, D. R.; Lee, S. T.; Fong, E. Human Epidermal Keratinocyte Cell Response on Integrin-Specific Artificial Extracellular Matrix Proteins. *Macromol. Biosci.* **2014**, *14*, 1125-1134). As a result of the cloning strategy, using Xho 1, Sal 1 and Nhe 1 restriction sites, several amino acids were altered within the recombinant ELP proteins (ELP16, ELP16-HIS and ELP16-FLAG; SEQ ID NOs: 1-3) used herein. There are 4 additional amino acids at the N-terminus (MKVD); amino acids 55-56 and 361-362 are LD; amino acids 207-208 are AS. In addition, for ELP16 and ELP16-HIS, amino acids 413-414 are LE, whereas in ELP16-FLAG amino acids 413-414 are LD and an LE is on the C-terminus. M is a starting methionine; VD is a Sal 1 restriction site; LE is an Xho 1 restriction site; AS is an Nhe 1 restriction site and LD results from ligating Sal 1 and Xho 1. Bacteria BL21(DE3)pLysS cells were transformed with pET22b plasmid encoding the ELP16 gene *via* heat shock. Colonies were selected and grown in 50 mL TB (Terrific broth)

media containing 50 mg L⁻¹ ampicillin and 34 mg L⁻¹ chloramphenicol overnight. The next day, 10 mL of bacteria culture was re-inoculated into 1 L TB media containing the same antibiotics, and grown to an optical density at 600 nm (OD₆₀₀) of 0.7 – 0.8 at 37 °C. To induce protein expression, isopropyl β-D-1-thiogalactopyranoside (IPTG) was added to a final concentration of 1 mM. Bacterial cells were harvested after 4 h by centrifugation at 8000 rpm at 4 °C for 20 min before resuspending in TEN buffer (0.1 M Tris, 0.01 M EDTA, 1 M NaCl). The cell mixture was sonicated on ice and subsequently centrifuged at 4 °C to collect the supernatant. The ELP16 was purified *via* inverse thermal cycling as previously described (Tjin, M. S.; Chua, A. W. C.; Ma, D. R.; Lee, S. T.; Fong, E. Human Epidermal Keratinocyte Cell Response on Integrin-Specific Artificial Extracellular Matrix Proteins. *Macromol. Biosci.* **2014**, *14*, 1125-1134). Purified ELP16 was dialyzed against water for 3 days and lyophilized. Lyophilized ELP16 proteins were stored at -20 °C for further use.

As noted above, the recombinant ELP16 proteins were readily purified by inverse temperature cycling to give a very high yield of 1 g lyophilized product per 9 L culture.

Synthesis of LVP/NVP 3D porous nanostructures

Purified ELP16 was dissolved in cold distilled water (dH₂O). Soluble precursors LiH₂PO₄/NaH₂PO₄ and NH₄VO₃ were dissolved in 60 °C dH₂O with stirring to achieve a concentration of 0.3 M and 0.2 M respectively. The LVP/NVP precursors were cooled on ice, and added to the ELP16 solution with vigorous stirring on ice. The final concentration of ELP16 in the mixture was 7.5% wt/vol, and 125 mM, 187.5 mM for NH₄VO₃ and MH₂PO₄ respectively. The mixture was then kept stagnant for 1 h, and subsequently frozen in liquid nitrogen before lyophilization. The resulting sample was annealed at 750 °C for 10 h under argon atmosphere. Minute amounts of HNO₃ acid were added to the NVP precursor solution before mixing with ELP16 to avoid precipitation at low temperature.

LVP

From the XRD spectrum of the as-annealed sample (Figure 4A), characteristic peaks of well-crystallized Li₃V₂(PO₄)₃ (JCPDF no. 04-012-2044) could be seen. The Al peak was from the sample holder. There are no detectable impurity phases, indicating that we had successfully obtained pure crystalline Li₃V₂(PO₄)₃. Figure 5A shows the FESEM image of the as-synthesized 3D LVP foam (abbreviated as LVP@C/CAs). From the image, it was clear that the annealed product consisted of a nanofibrous porous network structure. FESEM images at higher magnifications (Figure 5B) also revealed that the micropores were around 3 μm in

diameter. The surfaces of the nanofibers were completely covered by LVP nanoparticles (Figure 5C). TEM images at low magnification (Figures 6A – B) show the inter-connected fibrous carbon matrix containing the LVP nanoparticles, confirming the formation of the aerogel structure. Figure 5D shows the TEM image of the nanofibers. LVP nanoparticles with diameters of about 100 – 200 nm were found to be embedded within the carbon matrix. Under higher magnifications (Figure 5E), it was clear that the LVP nanoparticles were encased by an amorphous carbon shell of around 5 nm thick, with the observed lattice spacing of 3.65 Å corresponding to the (211) plane of LVP. The carbon shell was probably from the pyrolysis of ELP16. The ELP16 scaffold was degraded into carbon matter during the annealing step, resulting in the carbon coating outside LVP nanoparticles and formation of a 3D conductive carbon porous matrix. This carbon matrix allowed the LVP nanoparticles to nucleate and grow at high temperatures without aggregation. The overall carbon content derived from the recombinant ELP16 matter was determined by dissolving the as-synthesized product in hot concentrated HCl and weighing the residual carbon. It was found that it contained about 22 wt% carbon. BET results of the product (Figure 7A) indicated that large amount of mesopores existed within the fibrous carbon matrix, with a specific surface area of 106.3 m² g⁻¹ and a narrow pore size distribution centered at 4 nm. Here, we conclude that hierarchically micro/meso-porous LVP@C/CAs nanostructures were indeed obtained.

NVP

To demonstrate the generality of our approach, we applied the same synthesis procedure to yield 3D NVP foams (abbreviated as NVP@C/CAs). The XRD results (Figure 4B) indicated that indeed pure crystallized Na₃V₂(PO₄)₃ (JCPDF no. 96-222-5133) was obtained. Figures 5F – H show the FESEM images of the annealed NVP 3D foams. The morphologies of the foams were similar to that of the LVP@C/CAs 3D foams shown in Figures 5A – C. The NVP 3D foams also consisted of a nanofibrous micro-porous network, covered by NVP nanoparticles. TEM images at low magnification (Figures 6C – D) also show similar aerogel structures found in LVP@C/CAs. Figure 5I is a TEM image of the fibers, clearly showing the presence of NVP nanocrystallites embedded within a carbon matrix. The NVP nanoparticles with diameters less than 200 nm were also encased by an amorphous carbon shell of around 5 nm thick, with the measured lattice spacing of 4.42 Å corresponding to the (104) plane of NVP (Figure 5J). BET results (Figure 7B) indicated that the specific surface area of NVP@C/CAs is 131.9 m² g⁻¹ and the pore size distribution is centered at 3 nm. Here, we demonstrated that micro/meso-porous NVP@C/CAs nanostructures could also be successfully fabricated via the same strategy.

Further Studies

To understand the mechanisms involved in the synthesis process, four separate mixtures containing (1) ELP16 and both precursors, (2) ELP16 and LiH_2PO_4 , (3) ELP16 and NH_4VO_3 , and (4) ELP16 only were prepared at 4 °C and freeze dried. Samples were immediately examined under FESEM. For ELP16 and both precursors, ELP16/ LiH_2PO_4 and ELP16/ NH_4VO_3 mixtures, fibrous porous structures were obtained (Figures 8A – C). However, in the absence of either LiH_2PO_4 or NH_4VO_3 , we were unable to obtain any nanofibers (Figure 8B and 8C). Instead, the sample collapsed into fine powder after annealing. Taken together, it is likely that interactions between LiH_2PO_4 , NH_4VO_3 and ELP16 facilitated the formation of the nanofibrous network. Our FTIR results shown in Figure 8D revealed shifts in the characteristic peaks for P-O stretching (*i.e.*, from 1179 cm^{-1} to 1150 cm^{-1}) and V-O-V stretching (from 942 cm^{-1} to 967 cm^{-1}) when LVP precursors were mixed with ELP16. Both results suggest that there were indeed interactions between H_2PO_4^- ions and ELP16 as well as between VO_3^- ions and ELP16. In addition, there were also shifts in peaks for C-NH₂ stretching (from 1234 cm^{-1} to 1260 cm^{-1}). Therefore, the interactions between H_2PO_4^- ions and ELP16 were likely due to hydrogen bonding between P-O-H and H-N-H, since there are 16 lysine residues (and hence 16 amine groups) per ELP16 molecule (Figure 1). The hydrogen bonding reduced the polarity of P-O bond and resulted in the shifts of P-O stretching peaks. On the other hand, interactions between VO_3^- ions and ELP16 could be due to the formation of dative bonds from the vacant electron orbitals of VO_3^- and the lone pairs of the -NH₂ on ELP16. Both interactions contributed to the shift in the characteristic peaks for C-NH₂ stretching to higher wavenumbers by increasing the polarity of C-N bond. Therefore, the possible mechanisms involved is proposed as follows. In pure ELP16 solutions, there exists hydrophobic forces stemming from the presence of hydrophobic residues along the ELP16 backbone (Figure 1). These hydrophobic forces coacervate the ELP16 molecules together. Meanwhile, an electrostatic repulsion force also exists between dissociated -NH₂ groups on the lysine residues. This electrostatic repulsion force acts to disperse the ELP16 molecules. When both forces cancel each other (as in the case of ELP16 only mixtures), nanofibers could not be formed. However, when LVP or NVP precursors are present, H_2PO_4^- and/or VO_3^- ions could bind to the -NH₂ groups in ELP16 and act as crosslinkers between two adjacent ELP16 molecules. These interactions are further strengthened by the formation of hydrogen bonding or/and dative bonding, thereby enhancing the association of adjacent ELP16 molecules while reducing the dispersive effects of the electrostatic repulsion. Hence, interactions between the H_2PO_4^- and VO_3^- ions

and ELP16 drive the formation of ELP16 bundles. In addition, the recruitment of H_2PO_4^- and VO_3^- ions on the ELP16 backbone also contributed to an overall negative charge on the surface of the ELP16 bundles, and further facilitated the recruitment of M^+ ions. We also noted that the freeze drying step was critical to preserve the integrity of the structure, without which the micro-pore network could not be maintained (Figure 8B).

Electrochemical Measurements

The coin-type cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The electrodes were fabricated by mixing of 80 wt% LVP or NVP with carbon nanotube (10 wt%) and polyvinylidene difluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP) solvent, and then pasted onto the aluminium foils. The mass loading in electrodes was around 1.0 mg cm^{-2} . For LVP LIB cells, lithium foils were used as anodes and the electrolyte solution was made of 1M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1, w/w). For NVP NIB cells, sodium foils were used as anodes and the electrolyte solution was made of 1M NaClO_4 in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC). All cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage ranges of 3.0 – 4.3 V vs. Li^+/Li for LVP and 2.5 – 3.8 V vs. Na^+/Na for NVP.

The electrochemical performance of MVP 3D foams were examined by galvanostatic cycling in CR2032 coin-type cells. Metallic lithium and sodium foils were used as the counter electrodes for LVP and NVP cathodes respectively. Figure 10A – B show the initial charge-discharge voltage characteristics of the LVP and NVP cathodes at a rate of 1C, respectively. Insets in Figure 10A – B are their corresponding cycling performances. A rate of $n\text{C}$ corresponds to a full charge or discharge in $1/n$ hour. Here, 1C equals to the current density of 133 mA g^{-1} for LVP and 118 mA g^{-1} for NVP, respectively. The redox plateau potentials of $\text{V}^{3+}/\text{V}^{4+}$ are clearly observed at around 3.6, 3.7 and 4.1 V (vs. Li^+/Li) for LVP and ~ 3.4 V (vs. Na^+/Na) for NVP, corresponding to two lithium or sodium extraction/insertion, *i.e.*, $\text{M}_3\text{V}_2(\text{PO}_4)_3 \leftrightarrow \text{MV}_2(\text{PO}_4)_3$ ($\text{M} = \text{Li}$ and Na). The potential hysteresis was found to be less than 0.06 V, thereby implying an excellent reversibility for Li/Na ions removal and uptake. As a result, at 1C, initial discharge capacities of up to 129 and 112 mA h g^{-1} with Coulombic efficiencies (calculated from the discharge capacity/charge capacity) of 98% and 97% were achieved for LVP and NVP cathodes respectively. Both efficiencies were nearly equivalent to their theoretical values. It was noted here that the capacity contribution from the carbon is negligible in the voltage ranges of 3.0 – 4.3 V (vs. Li^+/Li) and 2.5 – 3.8 V (vs. Na^+/Na), and

hence, only the masses of active LVP and NVP were included when calculating the specific capacities. In addition, a near perfect capacity retention (~99.5%) was observed for both types of cathodes during 100 cycles (inserts in Figure 10A – B).

5 The key advantage of our 3D MVP cathodes is their excellent ultrafast charging/discharging performances, which are highly desirable for high-power LIB/NIB applications such as HEVs and EVs. The discharge voltage profiles of LVP and NVP obtained at discharge rates from 5C to 200C are shown in Figure 10C and 10D, respectively. The discharge capacities of LVP were found to be 121, 112, 105, 91 and 79 mA h g⁻¹ at discharge rates of 5, 10, 20, 50 and
10 100C (Figure 10C). More significantly, the LVP 3D foam cathodes were able to achieve a capacity of 66 mA h g⁻¹ (~50% of its theoretical capacity), even at an ultrahigh rate of 200C (which corresponded to a time of 18 s to fully discharge). This performance is nearly one order of magnitude larger than materials used in current battery cathodes. Likewise, the 3D
15 NVP cathodes were also able to deliver reversible capacities of 109, 104, 99, 87, 73 and 51 mA h g⁻¹ at rates of 5, 10, 20, 50, 100 and 200C (Figure 10D). Both materials synthesized in this work demonstrated ultrafast discharging properties, far superior than most state-of-the-art LVP and NVP cathodes reported in the literature (Tables 1 and 2). Our MVP cathodes also exhibit outstanding long-term high rate cycling performances. From Figure 10E, there were no obvious capacity losses for LVP and NVP cathodes over 1000 cycles at a rate of
20 100C.

Table 1 A comparison of our LVP@C/CAs to previously reported LVP cathodes in the voltage range of 3.0-4.3 V vs. Li⁺/Li.

	10 C	20 C	50 C	100 C	200 C
Our LVP@C/CAs	112*	105	91	79	66
Ref. 1				66	
Ref. 2	108				
Ref. 3		90 (15 C)			
Ref. 4		47			
Ref.5	105				
Ref.6	74				
Ref. 7		83			
Ref.8			85		
Ref.9			87 (30 C)		

* The unit is mAh g⁻¹

Table 2 A comparison of our NVP@C/CAs to previously reported NVP cathodes in the voltage range of 2.5-3.8 V vs. Na⁺/Na.

	10 C	20 C	50 C	100 C	200 C
Our NVP@C/CAs	104 *	99	87	73	51
Ref. 10					44
Ref. 11	81 (5 C)				
Ref. 12	95 (5 C)				
Ref. 13	45				
Ref. 14	39	20			
Ref. 15	83	74	60 (30 C)		

* The unit is mAh g⁻¹

5

Finally, to evaluate the possible applications of our LVP and NVP 3D foams as cathode materials, we calculated their power and energy densities based on the weight of cathode materials, working voltages and capacities at various rates. Figure 10F shows the Ragone plot for our materials, compared to current advanced LIB and NIB cathodes (normalized to the weight of cathode materials). The LVP cathodes prepared in this work were able to achieve a specific energy density of 450 Wh kg⁻¹ at a power density of 2.2 kW kg⁻¹, while maintaining an energy density of 205 Wh kg⁻¹ at an ultrahigh power density of 41 kW kg⁻¹. Similarly, the NVP cathodes prepared in this work were able to achieve gravimetric energies of 350 and 147 Wh kg⁻¹ at specific powers of 1.8 and 30 kW kg⁻¹ respectively. Notably, the maximum specific power densities achieved by our MVP cathodes are significantly higher than the current state-of-the-art active materials such as LiNi_{0.5}Mn_{0.5}O₂,³¹ CNT/FePO₄ nanowires,²⁰ LiFePO₄/C,³² LVP/C thin film,³³ Na₃Ni₂SbO₆,³⁴ and NVP/graphene.³⁵ Hence, we envisioned that the LVP and NVP 3D foams developed in this work have tremendous potential for use in demanding energy storage applications such as HEVs and EVs.

20

Plausible mechanisms enabling ultrafast charge/discharge properties of 3D LVP and NVP cathodes are illustrated as below.

(i) It is well known that nanoscale materials have exceptionally short ion (Li⁺ and Na⁺) transport lengths, leading to a short time constant t for ion diffusion. Taking the estimated values of ion diffusivity D ($\sim 10^{-10}$ cm² s⁻¹ for LVP and $\sim 10^{-11}$ cm² s⁻¹ for NVP),^{36, 37} the time t for Li⁺ and Na⁺ to diffuse over 100 nm (average particle size, L)

25

is estimated to be 1 and 10 s for LVP and NVP respectively, computed using the equation $t = L^2/D$. Thus, the limiting factor in the improvement of charge/discharge rate is the delivery of ions and electrons to the surface of our monodispersed LVP and NVP nanoparticles rather than solid-state ion transport.

(ii) Large surface area of electrodes ($106.3 \text{ m}^2 \text{ g}^{-1}$ for LVP@C/CAs, $131.9 \text{ m}^2 \text{ g}^{-1}$ for NVP@C/CAs) permits high contact area with the electrolytes (Figure 7 for BET measurements).

(iii) The 3D interconnected electrolyte-filled pore networks provide fast transport channels for the conductive ions.

(iv) The 3D nanoporous carbon monolith combined with the carbon-coating on the nanocrystals can further act as the electrolyte reservoir and as the electronic conductor. The carbon matrix allows fast migration of both Li^+/Na^+ and e^- to the active sites of each LVP/NVP nanoparticle. Therefore, favorable transport characteristics of the unique hierarchical structure with an efficiently mixed conducting 3D network are assumed to lead to the overall excellent power performance.

References for Tables 1 and 2

1. Zhang, X.; Böckenfeld, N.; Berkemeier, F.; Balducci, A. Ionic-Liquid-Assisted Synthesis of Nanostructured and Carbon-Coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ for High-Power Electrochemical Storage Devices. *ChemSusChem* **2014**, 7, 1710-1718.
2. Wang, S.; Zhang, Z.; Jiang, Z.; Deb, A.; Yang, L.; Hirano, S.-i. Mesoporous $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ @ CMK-3 Nanocomposite Cathode Material for Lithium Ion Batteries. *J. Power Sources* **2014**, 253, 294-299.
3. Kang, J.; Mathew, V.; Gim, J.; Kim, S.; Song, J.; Im, W. B.; Han, J.; Lee, J. Y.; Kim, J. Pyro-Synthesis of a High Rate Nano- $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Cathode with Mixed Morphology for Advanced Li-Ion Batteries. *Sci. Rep.* **2014**, 4.
4. Xu, J.; Chou, S.-L.; Zhou, C.; Gu, Q.-F.; Liu, H.-K.; Dou, S.-X. Three-Dimensional-Network $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Composite as High Rate Lithium Ion Battery Cathode Material and Its Compatibility with Ionic Liquid Electrolytes. *J. Power Sources* **2014**, 246, 124-131.
5. Fei, L.; Sun, L.; Lu, W.; Guo, M.; Huang, H.; Wang, J.; Chan, H. L.; Fan, S.; Wang, Y. Stable 4 V-Class Bicontinuous Cathodes by Hierarchically Porous Carbon Coating on $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Nanospheres. *Nanoscale* **2014**, 6, 12426-12433.
6. Zhang, C.; Li, H.; Ping, N.; Pang, G.; Xu, G.; Zhang, X. Facile Synthesis of Nitrogen-Doped Carbon Derived from Polydopamine-Coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as Cathode Material for Lithium-Ion Batteries. *RSC Adv.* **2014**, 4, 38791-38796.

7. Liu, Q.; Yang, F.; Wang, S.; Feng, L.; Zhang, W.; Wei, H. A Simple Diethylene Glycol-Assisted Synthesis and High Rate Performance of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Composites as Cathode Material for Li-Ion Batteries. *Electrochim. Acta* **2013**, *111*, 903-908.
8. Zhang, L.; Wang, S.; Cai, D.; Lian, P.; Zhu, X.; Yang, W.; Wang, H. $\text{Li}_3\text{V}_2(\text{PO}_4)_3@$
5 C/graphene Composite with Improved Cycling Performance as Cathode Material for Lithium-Ion Batteries. *Electrochim. Acta* **2013**, *91*, 108-113.
9. Mai, L.; Li, S.; Dong, Y.; Zhao, Y.; Luo, Y.; Xu, H. Long-Life and High-Rate $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Nanosphere Cathode Materials with Three-Dimensional Continuous Electron Pathways. *Nanoscale* **2013**, *5*, 4864-4869.
10. 10. Zhu, C.; Song, K.; van Aken, P. A.; Maier, J.; Yu, Y. Carbon-Coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Embedded In Porous Carbon Matrix: An Ultrafast Na-Storage Cathode with The Potential of Outperforming Li Cathodes. *Nano lett.* **2014**, *14*, 2175-2180.
11. Lim, S.J.; Han, D.W.; Nam, D.H.; Hong, K.S.; Eom, J.Y.; Ryu, W.H.; Kwon, H.S. Structural Enhancement of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Composite Cathode Materials by Pillar Ion Doping
15 for High Power and Long Cycle Life Sodium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 19623-19632.
12. Duan, W.; Zhu, Z.; Li, H.; Hu, Z.; Zhang, K.; Cheng, F.; Chen, J. $\text{Na}_3\text{V}_2(\text{PO}_4)_3@$ C Core-Shell Nanocomposites for Rechargeable Sodium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 8668-8675.
- 20 13. Nie, P.; Zhu, Y.; Shen, L.; Pang, G.; Xu, G.; Dong, S.; Dou, H.; Zhang, X. From Biomolecule to $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{Nitrogen-Decorated Carbon Hybrids}$: Highly Reversible Cathodes for Sodium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 18606-18612.
14. Liu, J.; Tang, K.; Song, K.; van Aken, P. A.; Yu, Y.; Maier, J. Electrospun $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Nanofibers as Stable Cathode Materials for Sodium-Ion Batteries. *Nanoscale*
25 **2014**, *6*, 5081-5086.
15. Jung, Y. H.; Lim, C. H.; Kim, D. K. Graphene-Supported $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as a High Rate Cathode Material for Sodium-Ion Batteries. *J. Mater. Chem. A* **2013**, *1*, 11350-11354.

Full Cell Performance

30

Method - Cell fabrications

The galvanostatic charge/discharge (GCD) performance of the synthesized LVP cathodes were tested using 2032 coin-type cells. The active electrode was fabricated by mixing 85%
35 active material (LVP or LTO (lithium titanate)) with 10% super-P conducting carbon and 5% polyvinylidene difluoride (PVDF). The active material loadings were about 3 to 5 mg range and the diameter of electrode was 14 mm. In order to obtain specific capacitance of the LVP

cathode, a half cell was assembled using LVP and Lithium metal as cathode and anode, respectively; a celgard polyethylene was employed as separator. 1M LiPF_6 in 1:1 (wt. %) ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte.

5 A similar procedure was used to fabricate the LTO based half cells in which LVP is replaced by an LTO anode material. In response to the half cell performance, a full cell configuration was assembled and tested. In detail, in the full cell configuration, LVP and LTO were used as cathode (positive) and anode (negative) electrodes respectively. Furthermore, the mass loading on both electrodes was adjusted according to the specific capacity of the half cell
10 performances. From these previous results, the mass loading of LVP and LTO were fixed at a 1.3:1 weight ratio. The separator and the electrolytes remain the same (above mentioned) in the full cell configuration. All the characteristic performances were limited with respect to the cathode materials (this is usual in the full cell) which means, the current rate, and the cell voltages were defined with respect to the LVP cathode. All the cells (half and full cells) were
15 tested in a moisture controlled argon-filled glove box ($\text{H}_2\text{O} < 0.1$ ppm; $\text{O}_2 < 0.1$ ppm). GCD performances at different current rates were performed using Neware™ battery tester in a desired voltage window.

Results and Discussion

20

Half Cell Performances of LVP and LTO

Figure 11a shows the charge/discharge performances of the LVP half cell configuration. The specific reversible capacity of the LVP was estimated as being 128 mAh/g at 0.1C; this value
25 is very close to the theoretical capacity (132 mAh/g) of the LVP cathode in a 4.3 V voltage window (two electron extractions). The first Li^+ is extracted in two steps because of the existence of an ordered phase LVP. Three corresponding discharge plateaus at 3.5, 3.65 and 4.1 V are signed as the reinsertion of the two lithium ions that accompanied the phase transition from $\text{LiV}_2(\text{PO}_4)_3$ to $\text{Li}_2\text{V}_2(\text{PO}_4)_3$, $\text{Li}_{2.5}\text{V}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, respectively. Figure
30 11b shows the charge/discharge performance of the LTO half-cell at 0.1 C at a voltage window of 1 to 3V. From the plot, it can be seen that the half cell showed a discharge capacity of 170 mAh/g and 155 mAh/g at 0.1 and 1C rate respectively.

LVP || LTO Full Cell Performance

35

The performance of full-cell using LVP and LTO as cathode and anode respectively was subsequently studied. Figure 12 represents the charge/discharge performance of the

LVPILTO full cell at different C-rates. The full cell was tested at 0.1C rate in a voltage window range from 1.3 to 3.3 V. It was noted that the cell showed an initial discharge capacity of 100 mAh/g at 0.1 C rate, which is almost 90% of its initial capacity obtained at 0.1C rate (Figure 12). This implies that the LVP based full cell delivered a very good performance even at a high current rate. The full cell showed an average plateau voltage around 2.3 V. Hence, the LVPILTO based cell is a potential candidate for use in many battery applications.

Example 2 - Formation of 3D Hierarchically Porous Carbon-Encapsulated Metal Oxide Nanoparticles and Characterisation Thereof

Materials Characterization

Powder X-ray diffraction (XRD, Shimadzu Powder) using Cu K α radiation was employed to identify the crystalline phase of the synthesized materials. The particle size and morphology were analyzed using field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). FESEM images were taken using JEOL Model JSM-7600F. TEM images were acquired using JEOL 2010F TEM, operated at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA, Q500) was carried out from room temperature to 600 °C at a heating rate of 10 K min⁻¹ in air. X-ray photoelectron spectroscopy (XPS, ESCALab 250i-XL & Thetaprobe A1333) was used to analyze the elemental content of the annealed samples.

Construction of plasmid pET22b containing the gene encoding for ELP16-His

Plasmid pET22b containing the gene encoding for ELP16-His (named pET-ELP16-His) was constructed by cloning the gene encoding for ELP16 from pET-ELP16 to a commercially purchased pET22b vector via Sall and XhoI double digestion and T4 ligase ligation.

Expression and purification of protein ELP16-His

Bacterial BL21(DE3)pLysS cells were transformed with pET-ELP16-His via heat shock. Colonies were selected and grown in 50 ml TB (Terrific broth) media containing 50 mg L⁻¹ ampicillin and 34 mg L⁻¹ chloramphenicol overnight. The next day, 10 mL of bacterial culture was re-inoculated into 1 L TB media containing the same antibiotics, and grown to an optical density at 600 nm (OD₆₀₀) of 0.7 - 0.8 at 37 °C. To induce protein expression, isopropyl β -D-1-thiogalactopyranoside (ITPG) was added to a final concentration of 1 mM. Bacterial cells

were harvested after 4 h by centrifugation at 8000 rpm at 4 °C for 20 min before re-suspending in TEN buffer (0.1 M Tris, 0.01 M EDTA, 1 M NaCl). The cell mixture was sonicated on ice and subsequently centrifuged at 4 °C to collect the supernatant. ELP16-His were purified via inverse thermal cycling as previously described.^[47] Purified protein was
5 dialyzed against water and lyophilized.

Synthesis of 3D hierarchically porous carbon-encapsulated metal oxides using crosslinked ELP16-His

10 Purified ELP16-His and Bis(sulfosuccinimidyl) suberate (BS3) were dissolved in cold deionised (DI) water separately. BS3 solution was added into the ELP16-His solution at 4 °C with molar ratio of BS3 to amino groups being 1.5:1 to ensure complete cross-linking. The final concentration of ELP16-His was 10% wt/vol. The mixed solution was pipetted between two pieces of ParafilmTM-coated glasses and allowed to crosslink overnight at room
15 temperature. The cross-linked protein was retrieved and freeze-dried. The freeze-dried scaffold was rinsed in concentrated $\text{Fe}(\text{NO}_3)_3/\text{Co}(\text{NO}_3)_2$ ethanol solution at room temperature for 1 h, washed briefly with water, freeze-dried and annealed in air at 300 °C for 30 min.

The recombinant ELP16-His protein (Figure 2), contains highly hydrophobic domains (V, P, G, I) and interspersed lysine (K) residues that serve as crosslinking sites.
20 Bis(sulfosuccinimidyl)suberate (BS3) was added to ELP16-His to crosslink adjacent lysine groups within the ELP16-His molecules via amine-mediated chemistry.^[36] Addition of BS3 also depressed the T_i of ELP16-His and resulted in aggregation of ELP domains when the mixture was placed at room temperature.

25 Figure 13a shows the FESEM image of ELP16-His scaffold after crosslinking. A micro-porous structure with inter-connected micro-spheres was obtained, suggesting that there was self-aggregation of ELPs within a highly cross-linked protein network. This self-aggregation process was likely driven by the hydrophobic nature of ELP16-His molecules in
30 water. Figure 13b shows the FESEM image of cross-linked ELP16-His after loading with Fe^{3+} and shows that the 3D porous structure was maintained, confirming the stability of the scaffold.

$\text{Fe}_3\text{O}_4@\text{C}$

35 The XRD pattern of the as-annealed sample (Figure 14a) confirmed that Fe_3O_4 was indeed obtained, though the particles may not be well crystallized. Further evidence for the chemical

composition of the product was provided by the high-resolution X-ray photoelectron spectroscopy (XPS) spectrum of Fe 2p (Figure 15). The peaks at 712 eV and 726 eV can be attributed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively, which are very close to the values for Fe₃O₄ reported in the literatures. It should be noted that no charge transfer satellite peak of Fe 2p_{3/2} at around 720 eV was detected, further confirming the formation of Fe₃O₄ containing Fe³⁺ and Fe²⁺. Figures 16a and 16b show the FESEM images of the annealed sample, showing the presence of inter-connected carbon micro-spheres with diameters around 6 μm with macropores of between 1 μm and 10 μm therebetween. The microstructure of the sample was further examined using TEM (Figures 16c-d). Clearly, Fe₃O₄ nanoparticles (around 5 nm) were uniformly embedded within a carbon matrix (named Fe₃O₄@C). As compared with metal oxides/carbon composites prepared by other processes, the dispersion of Fe₃O₄ nanoparticles in carbon matrix is highly homogeneous, which could be due to specific interaction of Fe³⁺ with ELP16-His molecules present within the crosslinked network. The well-dispersed Fe₃O₄ nanoparticles with small sizes are critical for enhancing sodiation/desodiation reaction kinetics. The carbon content in the sample was estimated to be 25% (see TGA result in Figure 17), and the surface area of the as-synthesized product was determined to be 30 m² g⁻¹ (see BET data in Figure 18). The carbon matrix derived from the pyrolysis of ELP16-His aided to prevent Fe₃O₄ nanoparticles from growing in size or aggregating. The porous carbon matrix can also buffer volume change caused by the sodiation/desodiation of Fe₃O₄, which is vital to improve the cycling stability of the electrode.

Co₃O₄@C

To demonstrate the generality of this approach, a similar synthesis procedure was applied to successfully prepare porous 3D scaffold loaded with Co²⁺ and Co₃O₄@C nanocomposites. (see XRD spectra in Figure 14b). Figure 19a shows a typical FESEM image of the annealed porous carbon-encapsulated Co₃O₄ composite (Co₃O₄@C). Likewise, the Co₃O₄@C composites displayed a similar morphology to Fe₃O₄@C as presented in Figure 16, consisting of meso-porous microspheres within an inter-connected network. Figures 19b and 19c present the TEM images of the sample. It can be observed that Co₃O₄ nanoparticles around 5 nm in size are also distributed homogeneously within the carbon matrix. The carbon content in the Co₃O₄@C composite is about 28% according to the TGA analysis (Figure 17), and the BET specific surface area of the as-synthesized product was determined to be 28 m² g⁻¹ (see BET data in Figure 18b). The morphology similarity of the two hybrid metal oxide/carbon composites demonstrate that the ELP16-His is an efficient template for synthesizing carbon-encapsulated well-dispersed metal oxide nanoparticles *via* the biochemistry process.

Electrochemical measurements

For battery testing, the electrode slurry was prepared by mixing the active material ($\text{Fe}_3\text{O}_4@\text{C}$ or Fe_3O_4), carbon nanotubes (CNT) and poly(vinylidene fluoride) (PVDF) thoroughly at a weight ratio of 70:20:10 in N-methylpyrrolidone (NMP) solvent. The slurry was pasted on copper foils followed by drying at 70 °C overnight to obtain the working electrodes. The mass loading in electrodes was around 1.0 mg cm⁻². The coin-type half cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. Sodium foils were used as counter/reference electrodes, Whatman GF/D microfiber filter paper was used as the separator, and 1 M NaClO₄ dissolved in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) was used as electrolyte. The coin-type half cells were tested by a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage range of 0.005-3.0 V. The cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) of half cells were carried out by an electrochemical workstation (Solartron, 1470E).

The electrochemical performance of the as-synthesized $\text{Fe}_3\text{O}_4@\text{C}$ composite was evaluated in coin-type half cells with sodium foil as the counter/reference electrodes. Figure 20a shows the cyclic voltammetric (CV) curves of the cell with carbon-encapsulated Fe_3O_4 anode cycled at a scan rate of 0.1 mV s⁻¹. During the first cathodic cycle, the peak at 1.0 V corresponded to the insertion of Na⁺ into Fe_3O_4 leading to the formation of $\text{Na}_x\text{Fe}_3\text{O}_4$. This process is irreversible, similar to that observed for Li⁺ insertion reaction. The peak at 0.6 V could be assigned to the extended conversion reaction from $\text{Na}_x\text{Fe}_3\text{O}_4$ to metallic Fe and the formation of the solid electrolyte interphase (SEI) layer (P. R. Kumar, Y. H. Jung, K. K. Bharathi, C. H. Lim, D. K. Kim, *Electrochim. Acta* 2014, 146, 503). In the anodic scan, the two broad peaks at 0.74 and 1.34 V corresponded to the two-step re-oxidation of metallic Fe to Fe_3O_4 . The two reduction peaks present in the first cycle merged into one located at around 0.78 V in the following cycles and the peak intensity dropped significantly, suggesting that irreversible reactions such as the formation of SEI layer occurred. In subsequent cycles, the reduction/oxidation peaks for the conversion reaction were found to stabilize and overlap, demonstrating a highly reversible sodiation/desodiation reaction after the activation during the first cycle. Notably, the CV profile of the cell was kept nearly unchanged except for the increasing area with increasing scanning rate (Figure 21), indicating that the cell was capable of responding to quick discharging and charging, and hence has potential for high-rate sodium storage. Figure 20b shows the typical galvanostatic charge-discharge profiles of the cell with $\text{Fe}_3\text{O}_4@\text{C}$ composite anode at a current density of 0.1 A g⁻¹, and the corresponding profiles of bare Fe_3O_4 and Fe_2O_3 nanoparticles were also plotted for

comparison. No obvious discharge plateaus could be observed from the curves. The first discharge capacity of $\text{Fe}_3\text{O}_4@\text{C}$ was 1338 mA h g^{-1} , higher than the theoretical capacity of Fe_3O_4 (924 mA h g^{-1}). The cell delivered a charge capacity of 657 mA h g^{-1} in the first cycle, showing a Columbic efficiency of 49.1 %. The irreversible capacity was mainly caused by the irreversible reactions of SEI film formation and/or electrolyte decomposition. In contrast, the first discharge and charge capacity of bare Fe_3O_4 nanoparticles is 1010 and 373 mA h g^{-1} at 0.1 A g^{-1} . Fe_2O_3 nanoparticle, which has a higher theoretical capacity of 1007 mA h g^{-1} , delivered 816 and 398 mA h g^{-1} at 0.1 A g^{-1} for the first discharge and charge capacity. Obviously, the capacity values of bare iron oxides are lower than the theoretical capacity, implying that iron oxides nanoparticles only partially participate in the conversion reaction because of the sluggish reaction kinetics. The rate performance of the cells is shown in Figure 20c. The cell with $\text{Fe}_3\text{O}_4@\text{C}$ electrode delivered specific charge capacities of 510, 425, 330, 246 and 163 mA h g^{-1} at 0.2, 0.5, 1, 2 and 5 A g^{-1} , respectively. In contrast, the cell with bare Fe_3O_4 electrode showed specific charge capacities of 154, 138, 120, and 94 mA h g^{-1} at 0.5, 1, 2, and 5 A g^{-1} , respectively, while bare Fe_2O_3 exhibited similar charge capacities of 124, 106, 91, and 66 mA h g^{-1} , which are much lower than those of $\text{Fe}_3\text{O}_4@\text{C}$. Besides, our $\text{Fe}_3\text{O}_4@\text{C}$ composite also shows significant capacity superior to other previously reported iron oxide-based materials for sodium storage (Table 3), confirming the unique architecture advantage of the 3D $\text{Fe}_3\text{O}_4@\text{C}$ nanocomposite for high-capacity and high-rate sodium storage.

Table 3 A comparison of our $\text{Fe}_3\text{O}_4@\text{C}$ to previously reported iron oxides anodes in sodium ion batteries.

Our $\text{Fe}_3\text{O}_4@\text{C}$	200 mA g^{-1}	500 mA g^{-1}	1 A g^{-1}
	510	425	330
Ref. 1	248 (83 mA g^{-1})		<100 (834 mA g^{-1})
Ref. 2	350	260	190
Ref. 3	250 (130 mA g^{-1})		
Ref. 4	474	418	
Ref. 5	<250 (15 mA g^{-1})		

* The unit is mAh g^{-1}

Notably, the capacity at a high current density of 2 A g^{-1} was comparable to or better than most carbonaceous materials reported (M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, S. Komaba, *Phys. Chem. Chem. Phys.* **2014**, 16, 15007; L. Fu, K. Tang, K. Song, P. A. van Aken, Y. Yu, J. Maier, *Nanoscale* **2014**, 6, 1384; H. G. Wang, Z. Wu, F. L. Meng, D. L. Ma, X.

L. Huang, L. M. Wang, X. B. Zhang, *Chemsuschem* **2013**, 6, 56; W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen, X. L. Ji, *J. Mater. Chem. A* **2013**, 1, 10662; and S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, *Adv. Funct. Mater.* **2011**, 21, 3859), suggesting a great potential of this composite as an anode material for SIBs. The capacity increased to 647 mA h g⁻¹, which was close to the value of the initial cycle when the current density was switched to 0.1 A g⁻¹. The cycling performances of the cell with Fe₃O₄@C electrode at 0.1 A g⁻¹ are shown in Figure 20d. As can be observed, the cell shows good performance stability. The Columbic efficiency of the cell increases significantly upon cycling, eventually reaching around 98 %. The cell delivers a specific capacity of 513 mA h g⁻¹ during the 60th cycle at 0.1 A g⁻¹. Even at a relatively high current density of 0.2 and 0.5 A g⁻¹ (Figure 20e), the Fe₃O₄@C electrode still exhibits promising cycling stability (309 mA h g⁻¹ during the 100th cycle at 0.5 A g⁻¹) and high Columbic efficiency (around 98%).

The superior performance of the current Fe₃O₄@C composite can be ascribed to the following reasons. First, the much smaller Fe₃O₄ grain size (5 nm) in the composite is highly beneficial to shorten the ion diffusion pathways and enhance the sodiation/desodiation reaction kinetics, thus delivering higher sodium storage capacity. Second, the porous carbon matrix (with a specific surface area of 30 m² g⁻¹) facilitates the quick infiltration of the electrolyte into the active materials and improves ion diffusion efficiency, which is another key reason for the high-rate performance of the Fe₃O₄@C composite. Third, the carbon matrix combined with the porous structure of the Fe₃O₄@C nanocomposite helped to buffer volume change during the sodiation/desodiation reaction and effectively mitigate the electrode microstructure fading. Otherwise, the electrochemical process for sodium storage would induce a very high volume change if Fe₃O₄ was fully involved in the conversion reaction. In addition, the aggregation of the Fe₃O₄/Fe nanoparticles is significantly suppressed due to the presence of the carbon matrix. In all, the physical characteristics of the Fe₃O₄@C materials provide good cycling stability and eventually excellent electrochemical performance of the Fe₃O₄@C composite electrode.

The Co₃O₄@C nanocomposite also exhibits good sodium storage capability due to the ability of the material to facilitate fast sodiation/desodiation reactions. Figure 22a shows the rate performance of the cell with Co₃O₄@C electrode. The cell delivered specific charge capacities of 583, 416, 310, 251, and 183 mA h g⁻¹ at 0.1, 0.2, 0.5, 1, and 2 A g⁻¹, respectively. The specific capacities at high current densities also outperformed other reported Co₃O₄-based materials for sodium storage (Table 4).

Table 4 A comparison of our $\text{Co}_3\text{O}_4@\text{C}$ to previously reported Co_3O_4 anodes in sodium ion batteries.

Our $\text{Co}_3\text{O}_4@\text{C}$	100 mA g^{-1}	200 mA g^{-1}	500 mA g^{-1}
	583	416	310
Ref. 6	293(34 mA g^{-1})		
Ref. 7	447 (25 mA g^{-1})		
Ref. 8	290 (58 mA g^{-1})		
Ref. 9	524 (25 mA g^{-1})		82
Ref. 10		390 (160 mA g^{-1})	

* The unit is mAh g^{-1}

- 5 In addition, the $\text{Co}_3\text{O}_4@\text{C}$ electrode also shows promising cycling performance, as shown in Figure 22b. The cell delivered a specific capacity of 228 mA h g^{-1} at 0.5 A g^{-1} during the 150th cycle with a high Columbic efficiency of 99%. The superior electrochemical performances of $\text{Co}_3\text{O}_4@\text{C}$ nanocomposites further confirm that carbon-encapsulated metal oxide nanoparticles are efficient anode materials for high-capacity, high-rate and durable sodium storage.

Conclusions

- 15 In this work, biochemistry routes were used to prepare carbon-encapsulated transition metal oxide nanoparticles (Fe_3O_4 and Co_3O_4). Using recombinant elastin-like polypeptides (ELP16-His) templates, we showed that metal precursors interact specifically with the protein microstructure to yield Fe_3O_4 and Co_3O_4 nanoparticles with 5 nm in diameter. After annealing, the protein matter degraded into a porous, carbonaceous matrix, encapsulating the Fe_3O_4 and Co_3O_4 nanoparticles. The carbon-encapsulated metal oxides demonstrated excellent sodium storage capability with high specific capacities, good rate capabilities and cycling stabilities. The cell delivered a specific charge capacity of 657 and 583 mA h g^{-1} at 0.1 A g^{-1} for carbon-encapsulated Fe_3O_4 and Co_3O_4 , respectively, while maintaining the charge capacities of 246 and 183 mA h g^{-1} at 2 A g^{-1} . In summary, we demonstrate a versatile biochemistry approach for the synthesis of highly efficient carbon-encapsulated metal oxide nanoparticles for sodium-based energy storage and conversion applications.

References for Tables 3 and 4

- [1] P. R. Kumar, Y. H. Jung, K. K. Bharathi, C. H. Lim, D. K. Kim, *Electrochim. Acta* **2014**, 146, 503.
- 5 [2] Z. Jian, B. Zhao, P. Liu, F. Li, M. Zheng, M. Chen, Y. Shi, H. Zhou, *Chem. Commun.* **2014**, 50, 1215.
- [3] M. Valvo, F. Lindgren, U. Lafont, F. Björefors, K. Edström, *J. Power Sources* **2014**, 245, 967.
- [4] Y. Jiang, M. Hu, D. Zhang, T. Yuan, W. Sun, B. Xu, M. Yan, *Nano Energy* **2014**, 5,
10 60.
- [5] S. Hariharan, K. Saravanan, V. Ramar, P. Balaya, *Phys. Chem. Chem. Phys.* **2013**, 15, 2945.
- [6] Q. Deng, L. Wang, J. Li, *Journal of Materials Science* **2015**, 50, 4142.
- [7] M. M. Rahman, A. M. Glushenkov, T. Ramireddy, Y. Chen, *Chem. Commun.* **2014**,
15 50, 5057.
- [8] J. W. Wen, D. W. Zhang, Y. Zang, X. Sun, B. Cheng, C. X. Ding, Y. Yu, C. H. Chen, *Electrochim. Acta* **2014**, 132, 193.
- [9] Y. Liu, Z. Cheng, H. Sun, H. Arandiyani, J. Li, M. Ahmad, *J. Power Sources* **2015**, 273, 878.
- 20 [10] Z. Jian, P. Liu, F. Li, M. Chen, H. Zhou, *J. Mater. Chem. A* **2014**, 2, 13805.

Example 3 - Formation of 3D Hierarchically Porous Carbon-Encapsulated Metal Oxide Nanocrystals and Characterisation Thereof**25 Materials Characterization**

The morphology of the as-prepared materials was examined using scanning electron microscopy (SEM, JSM 6340F) and transmission electron microscopy (TEM, JEOL, 2010UHR). X-Ray powder diffraction (XRD, Shimadzu powder, 40 kV/30 mA, Cu-Ka
30 radiation) was used to characterize the phases of the prepared materials. XPS (Thermo scientific ESCALAB 250) was used to identify the composition of the as-obtained material. The nitrogen adsorption–desorption isotherms was acquired using a ASAP Tri-star II 3020 analyzer, and the specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method (S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular
35 layers, *Journal of the American Chemical Society*, 60 (1938) 309-319; and J.B. Parra Soto, J. De Sousa, R.C. Bansal, J. Pis Martínez, Characterization of activated carbons by the BET equation: an alternative approach, *Adsorption Science and Technology*, 12 (1995) 51-66).

The pore size distribution was derived from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method (E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *Journal of the American Chemical society*, 73 (1951) 373-380.). FT-IR spectra were recorded on a Fourier transform infrared spectrometer (PerkinElmer) with a DGTS detector. TGA was performed on TA Instrument Q500.

Construction of ELK16-FLAG

The plasmid pET22b containing the gene encoding for ELK16 was obtained as described in Examples 1 and 2. To construct ELK16-FLAG, DNA oligomers encoding for the FLAG sequence (CDYKDDDDKL) were purchased (IDT, Singapore) and annealed. Complementary strands of DNA oligomers were separately dissolved in oligomer buffer (10 mM Tris) to final concentration of 1 $\mu\text{g}/\mu\text{L}$. Both strands were mixed in equal ratios in annealing buffer (100 mM NaCl, 100 mM MgCl_2) to achieve a final concentration of 1 mM. The mixture was immersed in boiling water for 5min and allowed to cool to room temperature overnight. The annealed DNA was recovered via gel electrophoresis and digested with Xho I and Sal I restriction enzymes. The digested oligomers were then ligated to pET22b containing the ELK16 sequence, and transformed in DH5 α *E. Coli* strain via heat shock. Colonies were picked and verified using DNA sequencing.

Expression of ELK16-FLAG

The pET22b plasmid containing ELK16-FLAG was transformed into BL21-(DE3)pLysS cells via heat shock. Colonies were selected and grown in 50 mL of TB (Terrific broth) media containing 50mgL⁻¹ ampicillin and 34mgL⁻¹ chloramphenicol overnight. The next day, 10 mL of bacteria culture was reinoculated into 1 L of TB media containing the same antibiotics and grown to an optical density at 600 nm (OD600) of 0.7 – 0.8 at 37 °C. After that, isopropyl β -D-1-thiogalactopyranoside (IPTG) was added with a final concentration of 1 mM to induce protein expression. Bacterial cells were harvested for another 4 h and collected by centrifugation at 8000 rpm at 4 °C for 20 min before resuspending in TEN buffer (0.1 M Tris, 0.01 M EDTA, 1 M NaCl). The cell mixture was sonicated on ice and subsequently centrifuged at 4 °C to collect the supernatant. The final ELK16-FLAG protein was purified via inverse thermal cycling as previously described hereinbefore. Purified ELK16-FLAG was dialyzed against water for 3 days and lyophilized. Lyophilized ELK16-FLAG proteins were stored at -20 °C for further use.

Synthesis of $\text{MnF}_2@N,F\text{-C}$

Lyophilized ELK16-FLAG was first dissolved in 100 μL cold dH_2O (10% (w/v)) before adding
5 bis(sulfosuccinimidyl)suberate (BS3) at 2.68 :1 (molar ratio of sulfo-NHS ester in BS3 to K in
ELK16-FLAG). The solution was mixed homogeneously before being pipetted onto a glass
slide covered with clean parafilm. The protein solution was covered with another glass slide
and allowed to crosslink at room temperature for 4 h. The glass slides were subsequently
10 removed, and the crosslinked hydrogel was rinsed in water twice and subsequently
lyophilized. The lyophilized product was either immersed in ionic liquid (BmimBF_4) followed
by $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ solution, or *vice versa* depending on the synthesis. The resulting product
was annealed at 600 $^\circ\text{C}$ for 4 h under an argon atmosphere.

The annealed foams were observed to contain pores with diameters of about 500 nm, and it
15 is observed that the surfaces of the scaffolds were homogeneously covered by nanoparticles
with diameters of less than 50 nm (Figures 23a – c). Further analysis using TEM confirmed
the presence of MnF_2 nanoparticles within the protein matrices; most of these nanoparticles
were about 5 nm in diameter. The nanoparticles were well-crystallized, and can be indexed
to the (111) crystal plane of tetragonal MnF_2 (Figures 23e – f and inset in Figures 23).
20 Notably, we observed graphitization of the surrounding carbon matrix, with lattice spacing of
0.37 nm.

Well-defined XRD peaks assigned to the tetragonal MnF_2 and orthorhombic MnF_2
respectively were detected from the as-prepared material as Figure 24a. The widened
25 nature of these peaks suggest that MnF_2 particles were nanocrystallites, consistent with our
SEM and TEM observations. We also observed a broad peak at around 20 – 25 $^\circ$, which can
be ascribed to the (002) plane of graphite (Figure 24a). A similar XRD spectra was also
obtained when the protein scaffold was annealed without the addition of ionic liquid and
 Mn^{2+} precursors (Figure 24a). Taken together, both XRD and TEM data confirmed that the
30 ELK16-FLAG protein scaffold was indeed converted to graphitized carbon, at a low
annealing temperature of 600 $^\circ\text{C}$.

Raman spectroscopy was used to determine the degree of graphitization in the sample. For
carbon materials, the G band is a characteristic feature of graphitic layers, and corresponds
35 to the tangential vibration of the carbon atoms. On the other hand, the D band corresponds
to disordered carbon or defective graphitic structures. The intensity ratio of these two peaks

(I_D/I_G) partially depends on the graphitization degree. Figure 24b shows the Raman spectra for $MnF_2@N,F-C$ (bold curve) and a N- and F-doped carbon scaffold as control (N,F-C control; dotted curve). For $MnF_2@N,F-C$ sample, a $I_D/I_G = 1.08$ was obtained, suggesting that a relatively good degree of graphitization exists within the sample, compared to the N,F-C control ($I_D/I_G = 0.93$).

The specific surface area of the as-prepared $MnF_2@N,F-C$ material was determined to be $93 \text{ m}^2 \text{ g}^{-1}$ using Brunauer–Emmett–Teller (BET), with pores centered around 4 nm and 25 nm (Figure 24c and inset). These nanopores were much smaller than the ones observed using SEM (Figures 23a – c), and were probably generated during the carbonization of the protein matrix. The content of MnF_2 in the hybrid nanostructure was also analyzed using TGA and was found to be about 22 wt% (Figure 25). TGA analysis of the ELK16-FLAG protein scaffold sample revealed that complete carbonization of the protein matrix could be achieved at 480°C (Figure 25).

X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental content of the annealed $MnF_2@N,F-C$ sample. Figures 24d – f show the C1s, N1s and F1s spectra respectively. The primary C1s peak could be resolved into three components centered at ~ 284.9 , 285.9 , and 287.1 eV , corresponding to sp²C-sp²C, N-sp²C and N-sp³C bonds respectively (Figure 24d). The N-sp²C and N-sp³C peaks were attributed to the C=O (binding energy of $287.5 \pm 0.5 \text{ eV}$) and C–O bonds (binding energy of 285.9 eV). Likewise, well deconvoluted O1s peaks ascribed to C=O (534.5 eV) and C–O (532.9 eV) were also found in high resolution XPS spectrum of O1s (Figure 26). The N1s XPS spectrum can be deconvoluted into three peaks representing pyridine-like (398.8 eV), pyrrolic (400.2 eV) and quaternary N (401.2 eV) (Figure 24e). The N/C weight ratio in the scaffold was calculated to be 11.19% ($7.6\% / 67.9\%$) as shown in Table 5. And the ratio between each type of nitrogen was about 2.5:1:1 (pyridine-N: pyrrolic-N: quaternary N) in the final product. The overall atomic weight of N in the scaffold of $MnF_2@N,F-C$ anode was calculated to be 7.6% (Table 5). Figure 24f shows the high resolution XPS spectrum of F1s; two peaks could be ascribed to C-F bond (689.8 eV)^[41] and Mn-F bond (686.1 eV)^[42] respectively. The overall content of fluorine present in the carbon matrix was calculated to be 4.1% and the ratio of F-C to F-Mn was ca. 1:1.3 ($43.4\% / 56.6\%$) (Table 5). Hence, our XPS results confirmed that both nitrogen and fluorine were successfully doped into the carbon matrix.

Sample	S_{BET} [m ² g ⁻¹]	Theoretical elemental analysis (based on protein sequence)				XPS (experimental data)				% of total F1s		Specific capacity (mAh/g)	
		C%	N%	O%	H%	C%	N%	O%	F%	F-C	F-Mn	0.1C	10C
MnF ₂ @N, F-C	93.9	55.0	17.3	19.5	8.2	67.9	7.6	20.0	4.1	43.4	56.6	694	190
N,F-C control	41.5	55.0	17.3	19.5	8.2	-	-	-	-	-	-	356	73
N-C control	39.2	55.0	17.3	19.5	8.2	-	-	-	-	-	-	244	10

Table 5. Physical properties and electrochemical performance of the prepared materials

Interestingly, the morphology of the annealed sample was found to be significantly different than that of the original crosslinked protein scaffolds. Figure 27a is a SEM image of crosslinked, freeze-dried protein scaffold showing irregular pores of several microns in diameter. We found that if the crosslinked scaffold was treated with ionic liquid before adding Mn²⁺ (i.e., IL (4 h)/ 1 M Mn²⁺ (4h) / IL (overnight)), the macropore structures of the freeze-dried scaffold were maintained, albeit with their diameters reduced (Figure 27b). However, freeze-dried scaffolds treated first with Mn²⁺ (i.e., Mn²⁺ (4h) / IL (4 h)/ Mn²⁺ (overnight)) were unable to maintain their porous structures after annealing (Figures 27c-d). Hence, it is likely that low pH of MnCl₂·4H₂O precursors (pH ~ 4.5) resulted in excessive swelling of the protein scaffold, and subsequent volume shrinkage during the carbonization of protein backbone in the annealing process. Both events could have led to the dramatic reduction of porosity in the final structure.

Formation of MnF₂ crystals was also dependent on the presence of the FLAG tag (CDYKDDDDKL). In a separate control where the FLAG tag was removed (i.e., ELK16), we were unable to obtain any MnF₂ crystallites. We were also unable to obtain similar porous structures compared to ELK16-FLAG. Figures 28a – b show the SEM images of the as-annealed product using crosslinked ELK16 as the starting scaffold. We were also unable to detect any MnF₂ peaks in the XRD spectrum of the annealed product (Figure 28c), where instead, a dense graphitized carbon matrix was observed (Figure s 27d – e). Hence, we conclude that the carboxyl-rich CDYKDDDDKL sequence played a critical role in the formation of MnF₂ crystals. It is plausible that the negative charges presented on the FLAG tag serve to recruit Mn²⁺ ions to increase the local concentration of Mn²⁺ for reaction with F⁻ ions within the protein matrix. This could account for the formation of well-crystallized MnF₂ at the low annealing temperature of 600°C.

Electrochemical Measurements

The electrochemical performances of the prepared material as anode for rechargeable lithium batteries were examined in coin type cells. The working electrodes were prepared by coating the slurry of the as-obtained active materials (90 wt%) and polyvinylidene difluoride (PVDF) (10 wt%) dissolved in N-methyl pyrrolidinone (NMP) onto a copper foil substrate and drying in a vacuum oven at 80 °C for 2 days. Then coin cells were fabricated using high-purity lithium foil as counter electrode and reference electrode, Celgard 2400 as the separator, and a solution of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1, in wt%) as the electrolyte. The assembly of the cells was conducted in an argon filled glove box with oxygen and water content less than 1 ppm. Galvanostatic charge–discharge measurements of fluoride anodes versus Li/Li⁺ were performed at room temperature under different rates (0.1–10 C) in a voltage range of 0.01 – 3.0 V on NEWARE multichannel battery test system. The current density used in the galvanostatically charged and discharged examination is calculated according to the theoretical capacity of 577 mA h g⁻¹ (2e⁻ transfer) for MnF₂ and based on the whole weight of MnF₂@N,F-C electrode. All electrochemical tests were performed at room temperature and the current density and specific capacity were calculated based on the prepared active materials.

The performance of the as-annealed 3D hybrid MnF₂@N,F-C as anodes in LIBs was evaluated. Figure 29a shows the discharge (Li insertion)/charge (Li extraction) curves of the MnF₂@N,F-C anode for the first four cycles at a rate of C/10. The MnF₂@N,F-C electrode delivered a reversible capacity as high as 679 mAh g⁻¹ during the first cycle, which is about 1.18 times of the theoretical capacity of MnF₂ (577 mAh g⁻¹). This value was also much higher than those of reported MnF₂ anodes (K. Rui, Z. Wen, Y. Lu, J. Jin, C. Shen, One - Step Solvothermal Synthesis of Nanostructured Manganese Fluoride as an Anode for Rechargeable Lithium - Ion Batteries and Insights into the Conversion Mechanism, *Advanced Energy Materials*, (2014); and Y.-H. Cui, M.-Z. Xue, K. Hu, D. Li, X.-L. Wang, W. SU, X.-J. Liu, F.-M. Meng, Z.-W. Fu, Electrochemical properties of MnF₂ films fabricated by pulsed laser deposition, *J Inorg Mater*, 25 (2010) 145-150). However, a reduced capacity of 408 mAh g⁻¹ was obtained following the first cycle, which could either be attributed to the formation of solid electrolyte interface (SEI) films on the surface of nanosized MnF₂ particles and carbon support, or due to the irreversible Li insertion into special positions such as the vicinity of residual H atoms. In addition, we also observed poorly defined plateaus at ~0.6 V, as a result of the conversion reaction between MnF₂ and Li, similar to what was reported for other nanocrystalline anodes. However, compared with bulk MnF₂, the observed plateau is

considerably short, which could be due to the increased surface areas within the nanostructured electrodes. Figure 29b shows the specific capacities of $\text{MnF}_2@\text{N,F-C}$ and control anodes (i.e., N,F-C and N-C). The $\text{MnF}_2@\text{N,F-C}$ anode was able to achieve high reversible capacities of about 694 mAhg^{-1} , 455 mAhg^{-1} , 392 mAhg^{-1} , 363 mAhg^{-1} , 343 mAhg^{-1} , 294 mAhg^{-1} , 264 mAhg^{-1} and 190 mAhg^{-1} at a discharge–charge rate of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C, 4C, 5 C and 10 C respectively (Figure 29c). $\text{MnF}_2@\text{N,F-C}$ delivered a capacity of 694 mAh/g , almost two-fold higher than N- and F-doped carbon (N,F-C; 356 mAh/g) or N-doped carbon (N-C; 244 mAh/g) control anodes. The significant increase in capacity was likely contributed by the presence of MnF_2 active materials within the carbon matrix in $\text{MnF}_2@\text{N,F-C}$. There was also significant improvement in the capacity due to F doping, comparing N,F-C and N-C control anodes.

$\text{MnF}_2@\text{N,F-C}$ anodes also showed good cycling stability at 10C for up to 2000 cycles, achieving a coulombic efficiency of nearly 100% (Figure 29d). In fact, the specific capacity of the anode increased to almost 350 mAhg^{-1} after 1000 cycles, similar to previous work on MnF_2 nanoparticles (K. Rui, Z. Wen, Y. Lu, J. Jin, C. Shen, One - Step Solvothermal Synthesis of Nanostructured Manganese Fluoride as an Anode for Rechargeable Lithium - Ion Batteries and Insights into the Conversion Mechanism, *Advanced Energy Materials*, (2014)). TEM images of the $\text{MnF}_2@\text{N,F-C}$ electrodes after 2000 cycles at 10C showed the breakdown of MnF_2 nanoparticles on the surfaces of carbon matrix (Figure 30). The breakdown of MnF_2 is characteristic of the conversion reaction between MnF_2 and Li. However, the broken down MnF_2 nanoparticles present in the discharged products were still able to facilitate electron transport via formation of conductive networks with the surrounding 3D graphitized carbon matrix. Hence, the hybrid structure $\text{MnF}_2@\text{N,F-C}$ electrodes led to the overall increase in capacity despite long cycling.

The capacity and rate performance of our $\text{MnF}_2@\text{N,F-C}$ electrodes were significantly better than previously reported MnF_2 (*ibid*). Their excellent rate performance could be attributed to enlarged contact areas between active materials and electrolyte and also reduced lithium-ion pathways resulting from the nanostructured architecture of the material. First, the porous structure and high surface area of the $\text{MnF}_2@\text{N,F-C}$ provides a high electrode/electrolyte contact area and a large number of active sites for charge-transfer reactions. Second, the small dimensions of the MnF_2 nanocrystallites in combination with the support of the 3D, porous graphitized carbon foam matrix facilitate mobilities of both Li^+ (short migration distance in the MnF_2 particles) and e^- (successive conductive network in the whole electrode) transportation; both events are critical to achieve high rate performance of the

electrode materials. Thirdly, the MnF_2 nanocrystals are encapsulated within the graphitized carbon matrix that provide efficient conductivity even for the non-conductive discharge product (such as LiF), thereby enhancing the reversibility of the electrode. Finally, the introduction of nitrogen and fluorine into carbon lattice further enhances carbon activity for Li storage, via incorporation of heteroatoms.

Conclusions

In this work, we demonstrate a biological route to prepare 3D N, F co-doped graphitized carbon foams containing MnF_2 nanocrystals ($\text{MnF}_2@N,F-C$). Recombinant elastin-like proteins were crosslinked to form a porous foam, and treated with ionic liquid and MnCl_2 . The annealed $\text{MnF}_2@N,F-C$ materials were evaluated as anodes for LIBs, and found to display a large reversible capacity, superior long-term cyclic performance and excellent rate performance. The unique architecture of the 3D $\text{MnF}_2@N,F-C$ foams resulted in large electrode/electrolyte contact area, increased active lithium storage sites and enabled rapid mass transport of electrons and Li ions. Hence, we show that biological routes are promising strategies for the synthesis of novel, hybrid 3D graphitized carbons containing active nanomaterials for energy storage applications.

Claims

1. A composite material comprising:
a nanofibrous carbon matrix substrate;
a nanocrystalline mixed-metal phosphate distributed throughout the nanofibrous carbon matrix substrate; and
an amorphous carbon coating on the nanocrystalline mixed-metal phosphate, wherein:

the amorphous carbon coating on the mixed-metal phosphate is from 1 nm to 10 nm thick, optionally from 2 nm to 7 nm, such as 5 nm;

the total carbon content of the composite material is from 1 wt% to 30 wt%, optionally from 5 wt% to 25 wt%, such as from 18 wt% to 22 wt%; and

the nanocrystalline mixed-metal phosphate has a diameter of from 100 to 300 nm and has a chemical composition according to formula I:



where:

x and z are independently 1 or 3; y is 1 or 2; A is Na or Li; and M is selected from V, Fe, Ni, Mn and Co,

provided that:

when M is selected from Fe, Ni, Mn and Co, then x, y and z are 1; and

when M is V, then x and z are 3, and y is 2.

2. The composite material according to Claim 1, wherein the carbon matrix contains both macropores and mesopores.
3. The composite material according to Claim 2, wherein:
- (a) the porous, nanofibrous carbon matrix substrate has a BET surface area of from $75 \text{ m}^2 \text{ g}^{-1}$ to $175 \text{ m}^2 \text{ g}^{-1}$; and/or
- (b) the nanocrystalline mixed-metal phosphate is homogeneously distributed throughout the carbon matrix substrate.
4. The composite material according to Claim 2 or Claim 3, wherein the mesopores in the carbon matrix have a pore size distribution centered at from 1 nm to 10 nm, optionally from 2 nm to 5 nm, such as from 3 nm to 4 nm, as measured using BET surface area analysis.

5. The composite material of any one of Claims 2 to 4, wherein:
 - (a) the mesopores have a diameter of from 1 nm to 20 nm, optionally from 2 nm to 10 nm, such as from 3 nm to 8 nm; and/or
 - (b) the macropores have a diameter of from 50 nm to 10 μm , optionally from 1 μm to 5 μm , such as from 2 μm to 4 μm .
6. The composite material according to any preceding claim, wherein the composition of formula I is $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ or $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.
7. A method of preparing a composite material according to any one of Claims 1 to 6, wherein the process comprises the steps of:
 - (a) providing an aqueous solution containing an elastin-like polypeptide that comprises lysine residues;
 - (b) adding one or more aqueous solutions containing mixed-metal phosphate precursor compounds to the solution containing the elastin-like polypeptide to form a conjugate mixture;
 - (c) freezing the conjugate mixture and lyophilizing it to provide a lyophilized conjugate; and
 - (d) annealing the lyophilized conjugate to provide a composite material according to any one of Claims 1 to 6.
8. The method according to Claim 7, wherein the annealing is conducted at a temperature of from 700°C to 900°C for from 1 hour to 24 hours, optionally at a temperature of from 750°C to 800°C for from 5 hours to 15 hours.
9. The method according to Claim 7 or Claim 8, wherein the elastin-like polypeptide that comprises lysine residues has the sequence $[(\text{VPGIG})_2\text{VPGKG}(\text{VPGIG})_2]_{16}$.
10. The method according to any one of Claims 7 to 9, wherein the concentration of the elastin-like polypeptide in the conjugate mixture is from 2.5% wt/vol to 20% wt/vol, optionally from 5% wt/vol to 10% wt/vol, such as 7.5% wt/vol.
11. The method according to any one of Claims 7 to 10, wherein the lyophilization is conducted by freeze-drying.
12. The method according to any one of Claims 7 to 10, wherein:

- (a) when the mixed-metal phosphate is $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, the mixed-metal phosphate precursors are NH_4VO_3 and LiH_2PO_4 ; and
 - (b) when the mixed-metal phosphate is $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, the mixed-metal phosphate precursors are NH_4VO_3 and NaH_2PO_4 .
- 13. The method according to Claim 12, wherein:
 - (a) the concentration of NH_4VO_3 in the conjugate mixture is from 100 mM to 150 mM, such as 125 mM; and
 - (b) the concentration of LiH_2PO_4 or NaH_2PO_4 in the conjugate mixture is from 175 mM to 200 mM, such as 187.5 mM.
- 14. The method according to Claim 12 or Claim 13, wherein before step (b) of Claim 7 is conducted:
 - (a) an aqueous precursor solution containing NH_4VO_3 is prepared having a concentration of 0.2 M; and
 - (b) an aqueous precursor solution containing LiH_2PO_4 or NaH_2PO_4 is prepared having a concentration of 0.3 M.
- 15. A cathode comprising a composite material according to Claims 1 to 7.
- 16. The cathode according to Claim 15, wherein the composite material comprises from 70 to 85 wt% of the cathode.
- 17. The cathode according to Claim 15 or Claim 16, wherein the cathode has one or more of the following properties:
 - (a) a potential hysteresis of less than 0.06 V;
 - (b) an initial discharge capacity of from 90 to 150 mA h g^{-1} at 1C;
 - (c) a columbic efficiency of from 95 to 99.5%;
 - (d) a capacity retention of from 98.0 to 99.9% during 100 charge/discharge cycles at 1C;
 - (e) a discharge capacity of from 50 to 80 mA h g^{-1} at 100C; and
 - (f) a capacity retention of from 98.0 to 99.5% during 1000 charge/discharge cycles at 100C.
- 18. A composite material comprising:
 - a nanofibrous carbon matrix substrate; and

nanoparticles of a metal oxide encapsulated within the nanofibrous carbon matrix substrate,

wherein:

the nanofibrous porous network structure has a BET surface area of from $20 \text{ m}^2 \text{ g}^{-1}$ to $40 \text{ m}^2 \text{ g}^{-1}$;

the total carbon content of the composite material is from 1 wt% to 30 wt%, optionally from 5 wt% to 29 wt%, such as from 22 wt% to 28 wt%;

the metal oxide has a diameter of from 1 nm to 15 nm and is selected from the group consisting of Fe_3O_4 , Fe_2O_3 , CoO , Co_3O_4 , NiO , MnO_2 , MnO , and Mn_2O_3 .

19. The composite material according to Claim 18, wherein:

(a) the carbon matrix contains macropores having a diameter of from 50 nm to 10 μm , optionally from 1 μm to 5 μm , such as from 2 μm to 4 μm ; and/or

(b) the nanofibrous carbon matrix has a BET surface area of from $25 \text{ m}^2 \text{ g}^{-1}$ to $32 \text{ m}^2 \text{ g}^{-1}$, optionally from $28 \text{ m}^2 \text{ g}^{-1}$ to $30 \text{ m}^2 \text{ g}^{-1}$; and/or

(c) the carbon matrix is composed of interconnected carbon microspheres having a diameter of from 2 μm to 10 μm , optionally from 4 μm to 8 μm , such as around 6 μm ; and/or

(d) the nanoparticles are homogeneously distributed throughout the carbon matrix.

20. The composite material according to Claim 18 or Claim 19, wherein the metal oxide is Fe_3O_4 or Co_3O_4 .

21. The composite material according to any one of Claims 18 to 20, wherein the nanoparticles of the metal oxide have a size of from 1 nm to 10 nm, optionally from 2 nm to 7 nm, such as 5 nm.

22. A method of preparing a composite material according to any one of Claims 18 to 21, wherein the process comprises the steps of:

(a) reacting an elastin-like polypeptide that comprises lysine residues and a metal conjugating group with a protein crosslinking agent and lyophilizing the resultant product to provide a lyophilised, cross-linked scaffold;

(b) rinsing the lyophilised, cross-linked scaffold with a metal oxide precursor solution to provide a first conjugate;

(c) washing the conjugate with water to form a washed conjugate;

- (d) freezing the washed conjugate and lyophilizing it to provide a lyophilized conjugate; and
- (e) annealing the lyophilized conjugate to provide a composite material according to any one of Claims 18 to 21.

23. The method according to Claim 22, wherein the annealing is conducted at a temperature of from 250°C to 400°C for from 15 minutes to 10 hours, optionally at a temperature of from 275°C to 325°C for from 30 minutes to 1 hour.

24. The method according to Claim 22 or Claim 23, wherein the elastin-like polypeptide that comprises lysine residues and a metal conjugating group has the sequence [(VPGIG)₂VPGKG(VPGIG)₂]₁₆HHHHHH.

25. The method according to any one of Claims 22 to 24, wherein the crosslinking agent is (bis)sulfosuccinimidyl suberate.

26. The method according to any one of Claims 22 to 25, wherein the molar ratio of the reactive group in the crosslinking agent to the lysine amino groups in the elastin-like polypeptide that comprises lysine residues and a metal conjugating group is from 1:1 to 10:1, such as 1.5:1.

27. The method according to any one of Claims 22 to 26, wherein the concentration of the elastin-like polypeptide in the reaction of step (a) of Claim 22 is from 5% wt/vol to 20% wt/vol, optionally from 7.5% wt/vol to 12.5% wt/vol, such as 10% wt/vol.

28. The method according to any one of Claims 22 to 27, wherein all lyophilization steps are conducted by freeze-drying.

29. The method according to any one of Claims 18 to 21, wherein:

- (a) when the metal oxide is Fe₃O₄, the metal oxide precursor is a solution of Fe(NO₃)₃ in a monohydric alcohol; and
- (b) when the metal oxide is Co₃O₄, the metal oxide precursor is a solution of Co(NO₃)₂ in a monohydric alcohol.

30. An anode comprising a composite material according to Claims 18 to 21.

31. The anode according to Claim 30, wherein the composite material comprises from 70 to 85 wt% of the anode.
32. The anode according to Claim 30 or Claim 31, wherein the anode has one or more of the following properties:
- (a) an initial discharge capacity of from 1000 to 1500 mA h g⁻¹ at 1 A g⁻¹;
 - (b) an initial charge capacity of from 500 to 700 mA h g⁻¹ at 1 A g⁻¹; and
 - (c) An initial columbic efficiency of from 40 to 50%.
33. A composite material comprising:
a N- and F-doped porous carbon matrix substrate; and
a nanocrystalline metal fluoride distributed throughout the porous carbon matrix substrate
wherein:
the metal fluoride is MnF₂;
the N:C weight ratio in the carbon matrix substrate is from 1:20 to 1:5, optionally from 1:10 to 1:6.67, such as from 1:9.09 to 1:8.33, as determined by X-ray photoelectron spectroscopy; and
the ratio of doped F to metal fluoride F is from 1:1 to 1:2, such as 1:1.3, as determined by X-ray photoelectron spectroscopy.
34. The composite material according to Claim 33, wherein the carbon substrate has a BET surface area of from 80 m² g⁻¹ to 110 m² g⁻¹, such as from 90 m² g⁻¹ to 95 m² g⁻¹.
35. The composite material according to Claim 33 or Claim 34, wherein the carbon matrix contains mesopores and macropores.
36. The composite material according to Claim 35, wherein:
- (a) the mesopores have a diameter of from 1 nm to 100 nm, optionally from 2 nm to 60 nm, such as from 3 nm to 50 nm, such as from 4 nm to 25 nm; and/or
 - (b) the macropores have a diameter of from 400 to 600 nm, such as around 500 nm.
37. The composite material according to Claim 36, wherein the mesopores have a first pore size distribution centered at from 1 nm to 10 nm, optionally from 2 nm to 5 nm, such as from 3 nm to 4 nm, and a second pore size distribution centered at from 15 nm to 35 nm, optionally from 20 nm to 30 nm, such as from 24 nm to 26 nm.

38. The composite material according to Claim 36, wherein the macropores have a pore size distribution centered at around 500 nm.

39. The composite material according to any one of Claims 33 to 38, wherein the intensity of disordered carbon: intensity of graphene carbon as measured using Raman spectroscopy is from 1:0.8 to 1:1, optionally from 1:0.90 to 1:0.95, such as 1:0.93.

40. A method of preparing a composite material according to any one of Claims 33 to 39, wherein the process comprises the following ordered steps of:

(a) reacting an elastin-like polypeptide that comprises lysine residues and a metal conjugating group with a protein crosslinking agent and lyophilizing the resultant product to provide a lyophilised, cross-linked scaffold;

(b) immersing the lyophilised cross-linked scaffold in a solution comprising an ionic fluoride source to provide a first conjugate;

(c) immersing the first conjugate in a solution comprising a water-soluble metal salt (e.g. a metal chloride) to provide a second conjugate;

(d) optionally freezing the second conjugate and lyophilizing it to provide a lyophilized conjugate; and

(e) annealing the second conjugate or lyophilized conjugate to provide a composite material according to any one of Claims 33 to 39.

41. The method according to Claim 40, wherein the annealing is conducted at a temperature of from 480°C to 700°C for from 1 hour to 10 hours, optionally at a temperature of from 575°C to 625°C for from 3 hours to 5 hours.

42. The method according to Claim 40 or Claim 41, wherein elastin-like polypeptide that comprises lysine residues and a metal conjugating group has the sequence [(VPGIG)₂VPGKG(VPGIG)₂]₁₆CDYKDDDDKL.

43. The method according to any one of Claims 40 to 42, wherein the crosslinking agent is (bis)sulfosuccinimidyl suberate.

44. The method according to any one of Claims 40 to 43, wherein the molar ratio of the reactive group in the crosslinking agent to the lysine amino groups in the elastin-like polypeptide that comprises lysine residues and a metal conjugating group is from 1:1 to 10:1, such as 2.68:1.

45. The method according to any one of Claims 40 to 44, wherein all lyophilization steps are conducted by freeze-drying.
46. The method according to any one of Claims 40 to 45, wherein:
- (a) the ionic fluoride source is BmimBF₄; and/or
 - (b) the metal chloride is MnCl₂.
47. An anode comprising a composite material according to Claims 33 to 39.
48. The anode according to Claim 47, wherein the composite material comprises from 85 to 95 wt% of the anode.

Figures

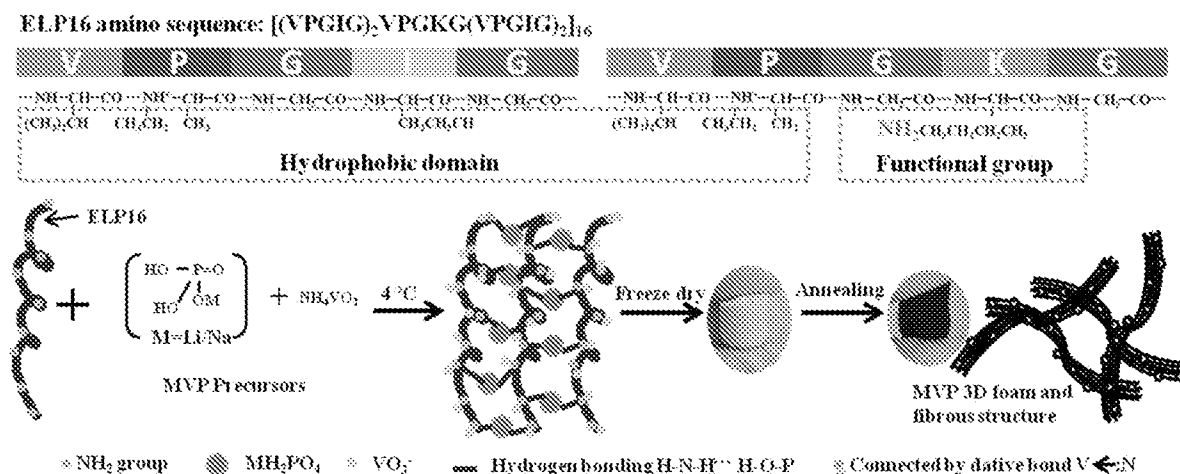


FIG. 1

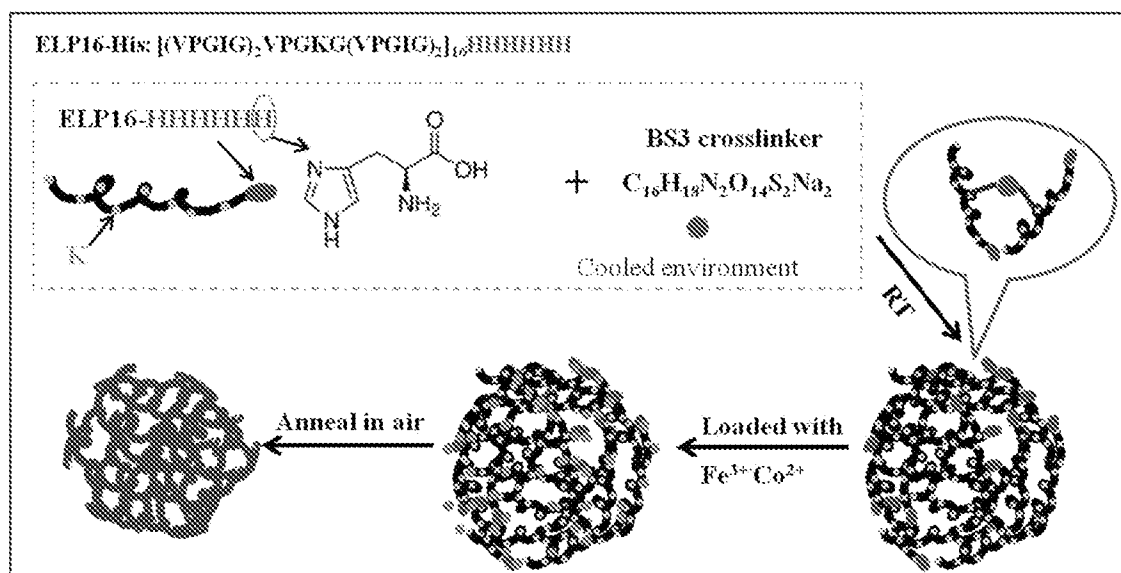


FIG. 2

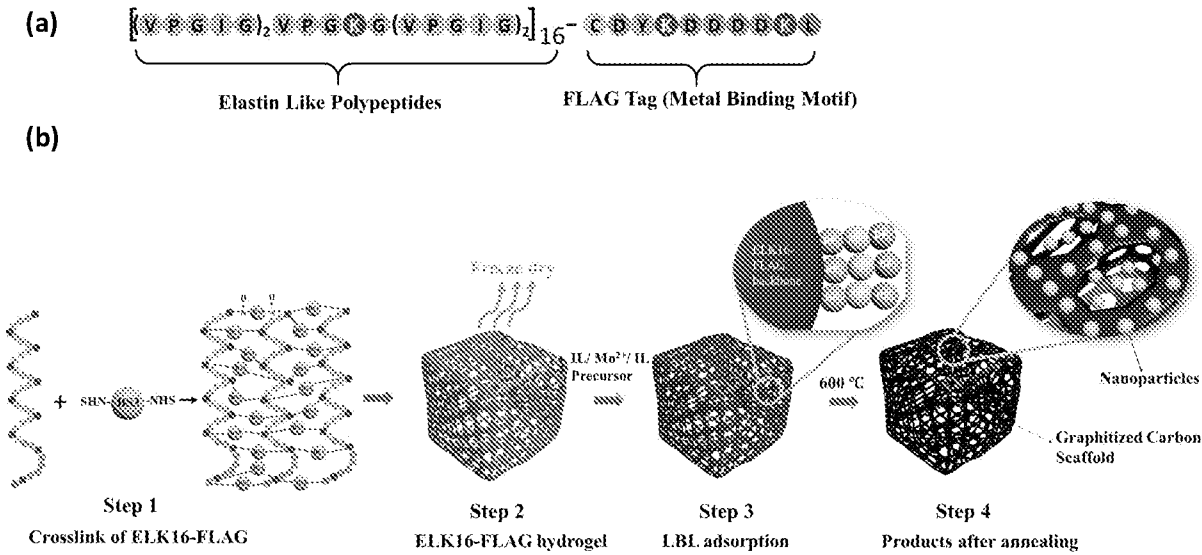


FIG. 3

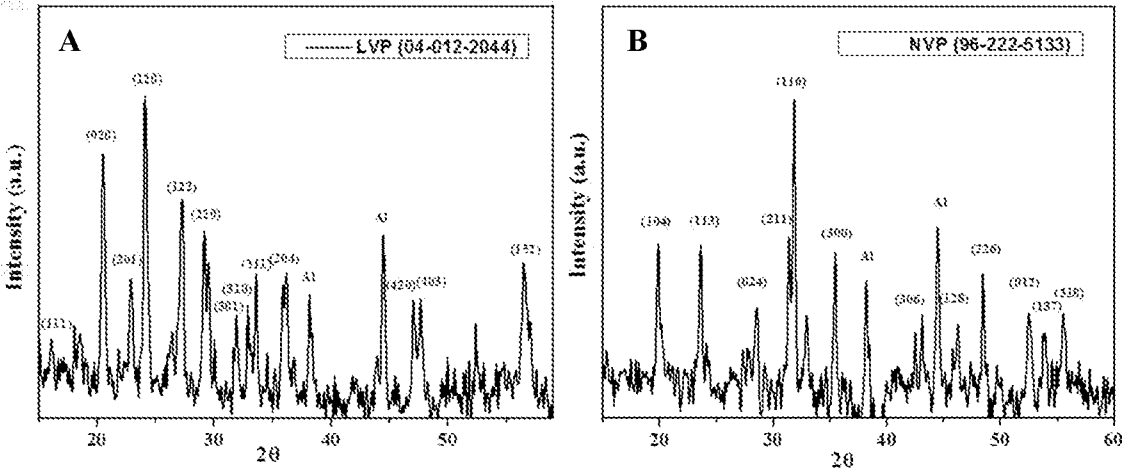


FIG. 4

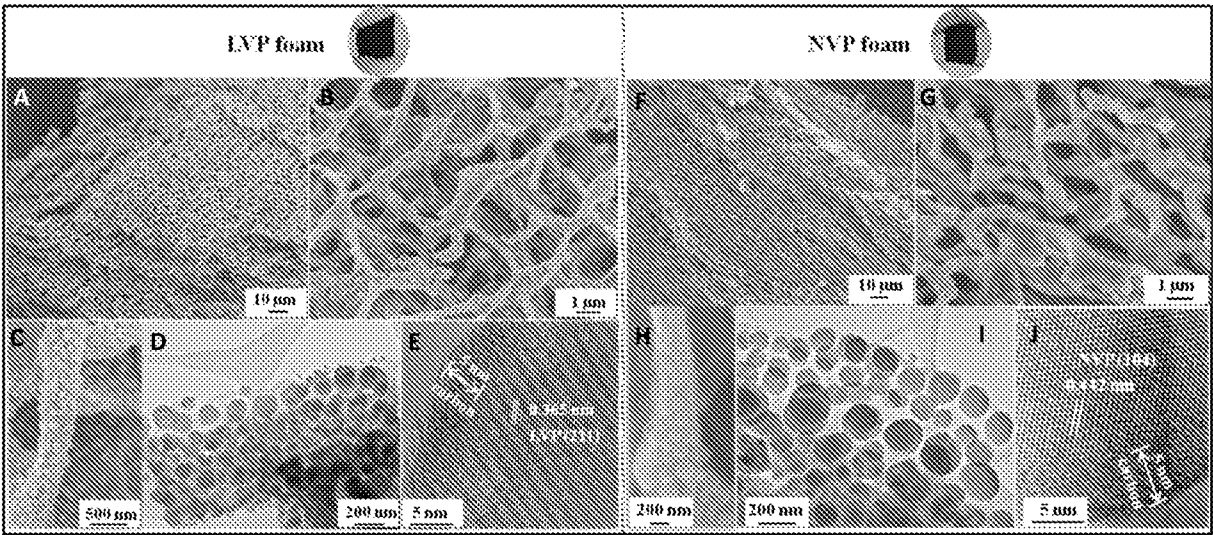


FIG. 5

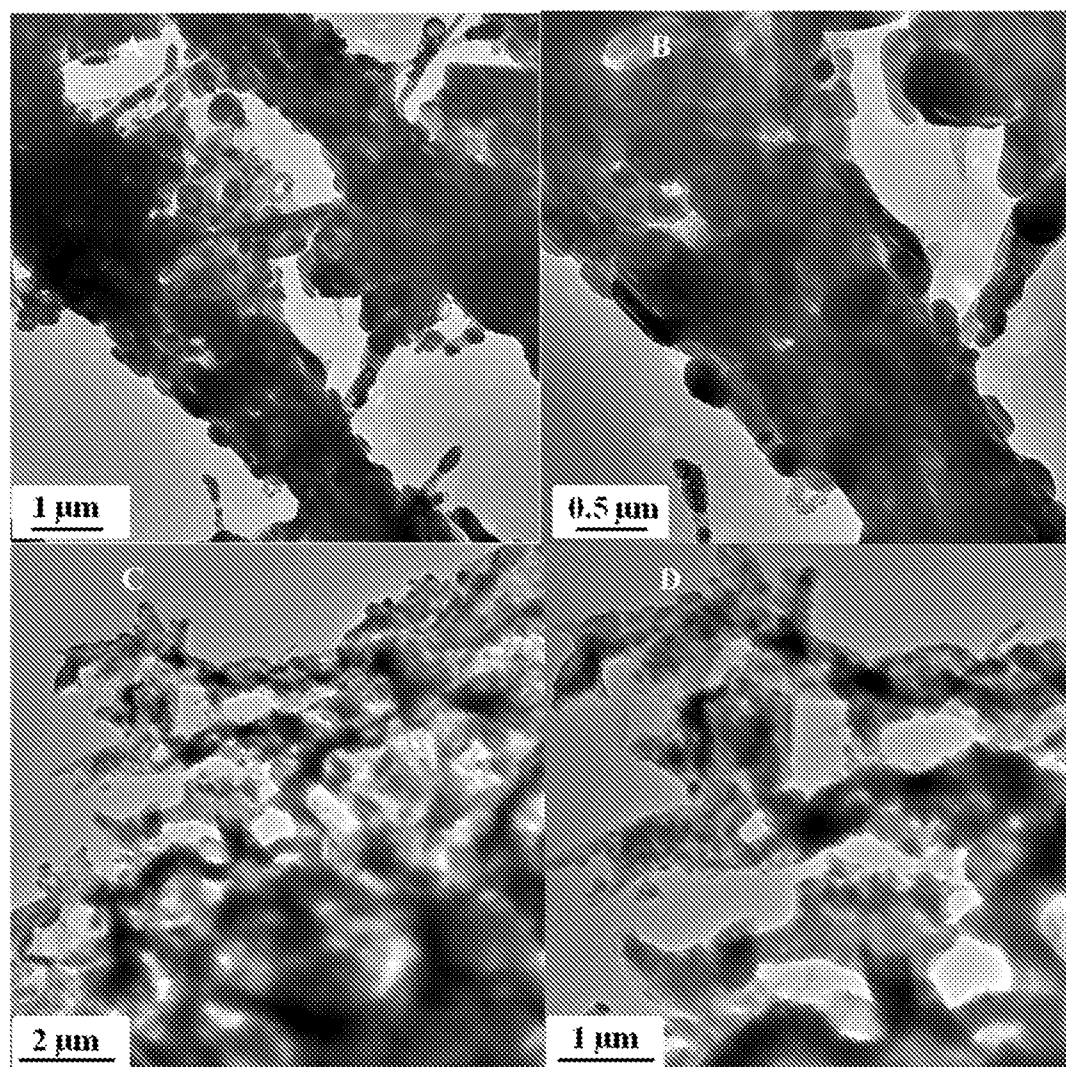


FIG. 6

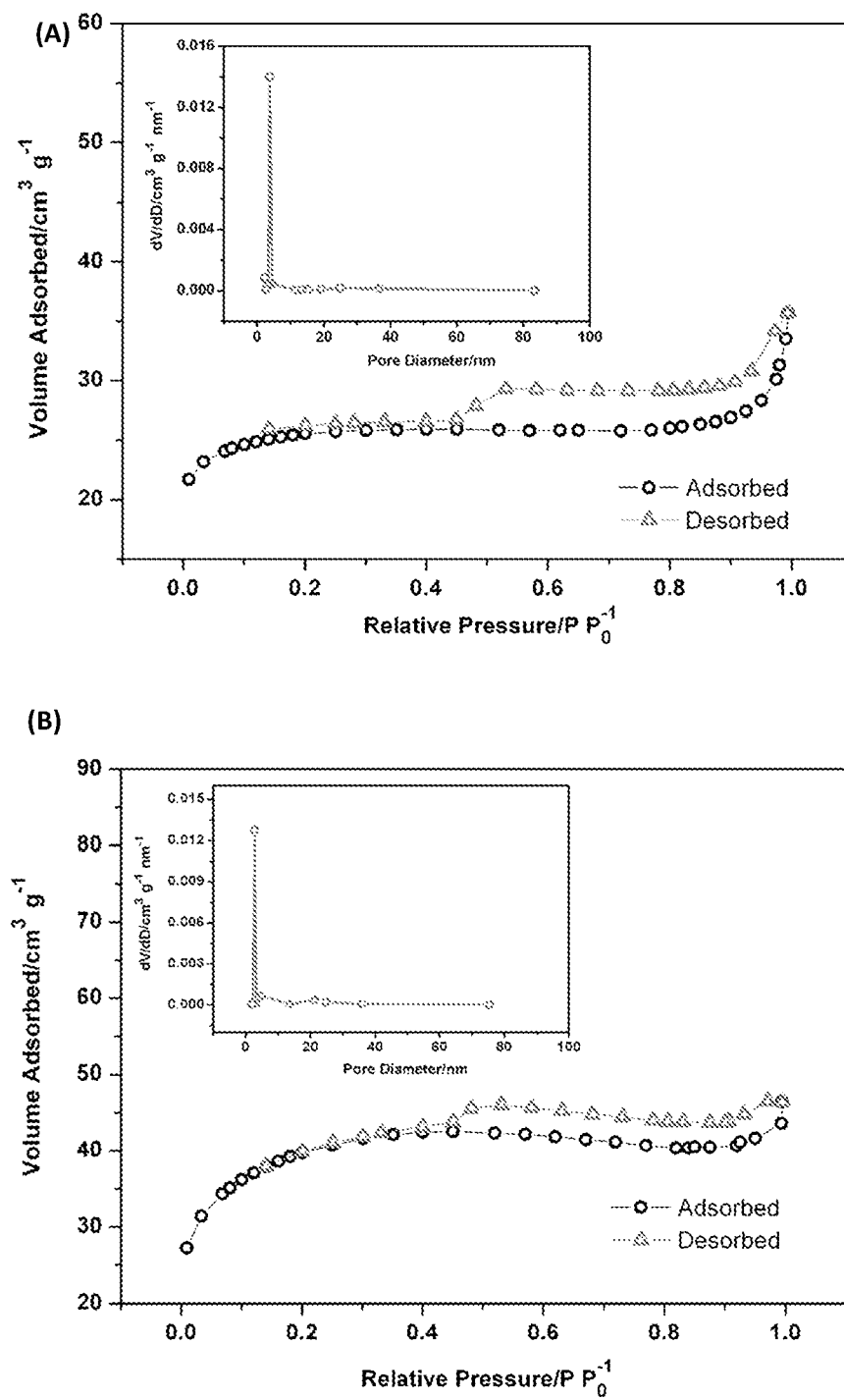


FIG. 7

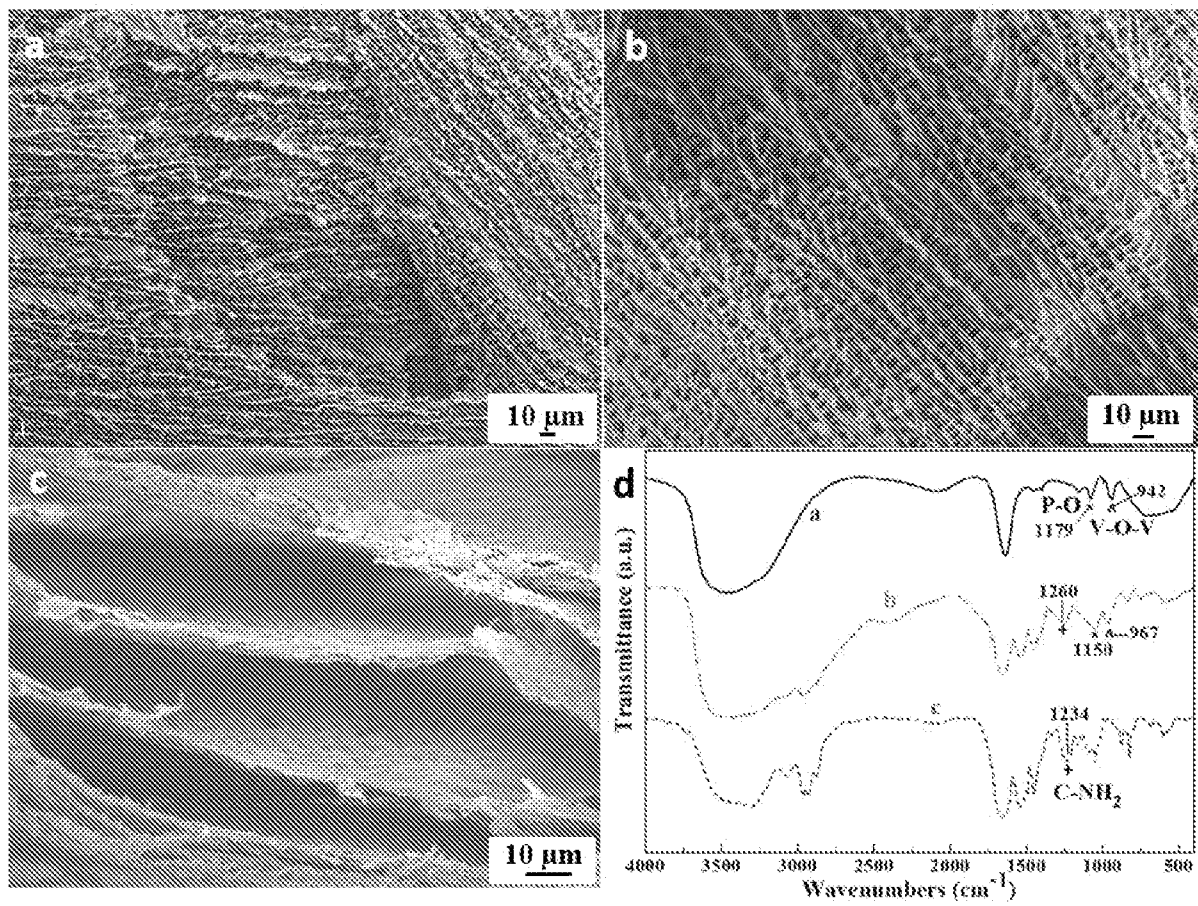


FIG. 8

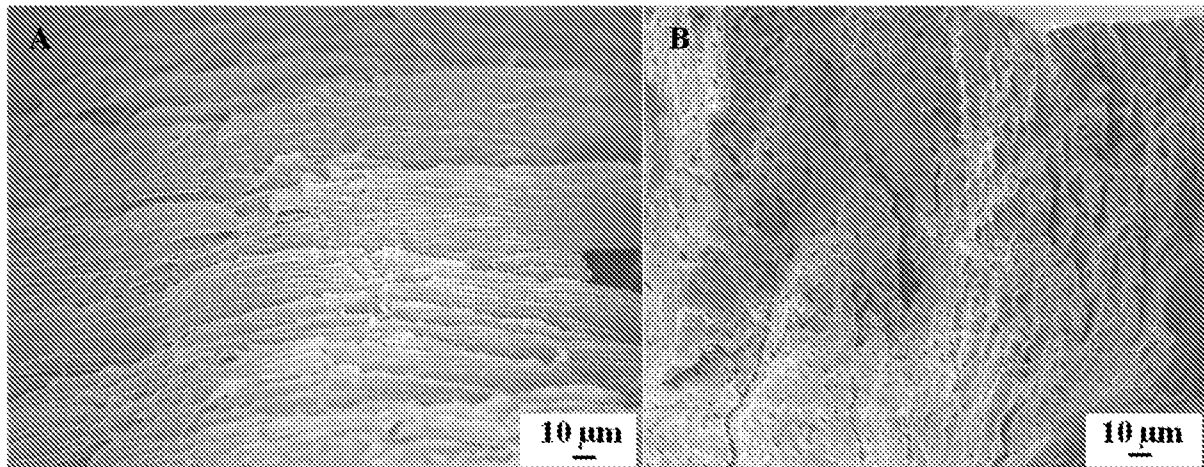


FIG. 9

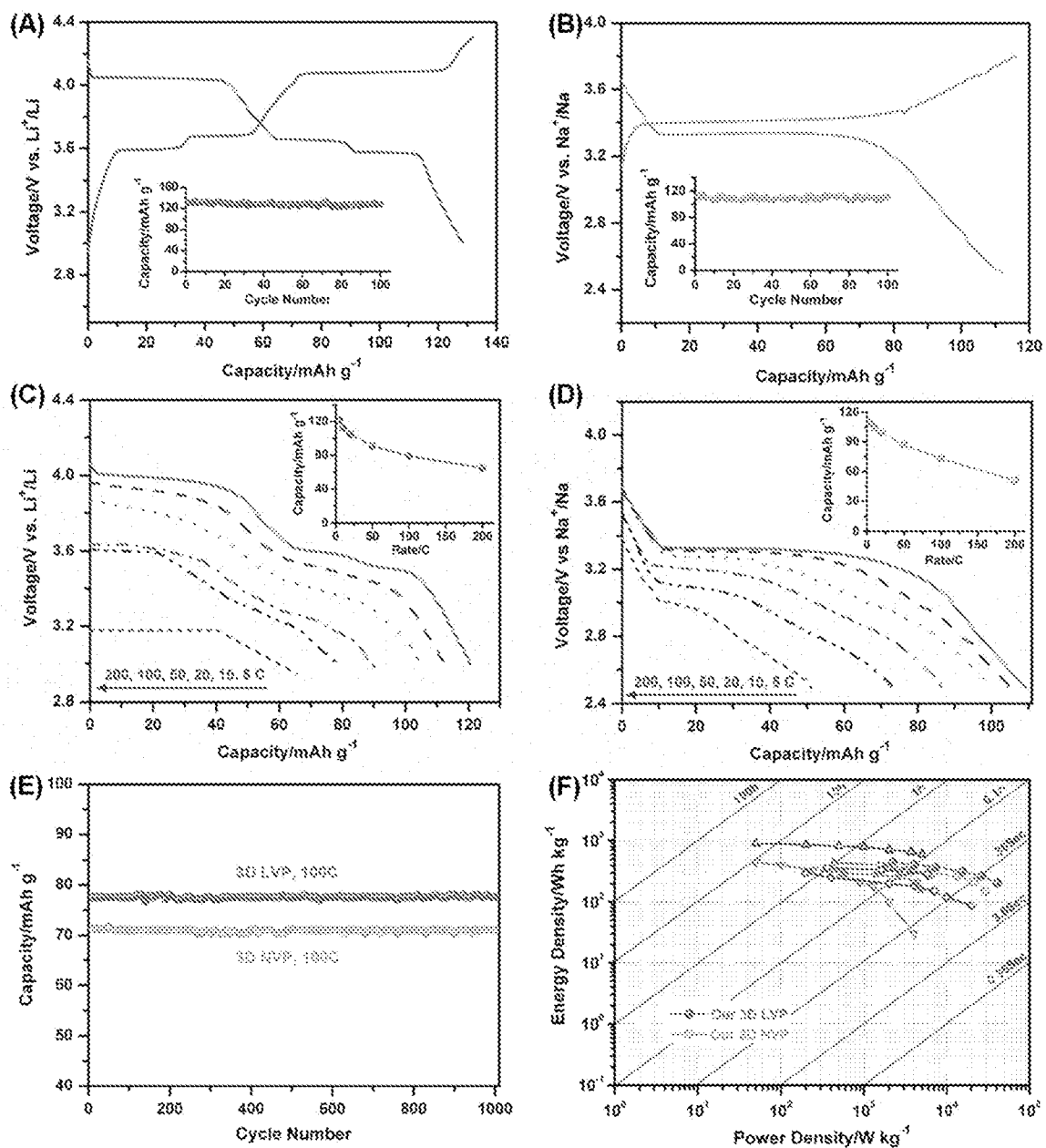


FIG. 10

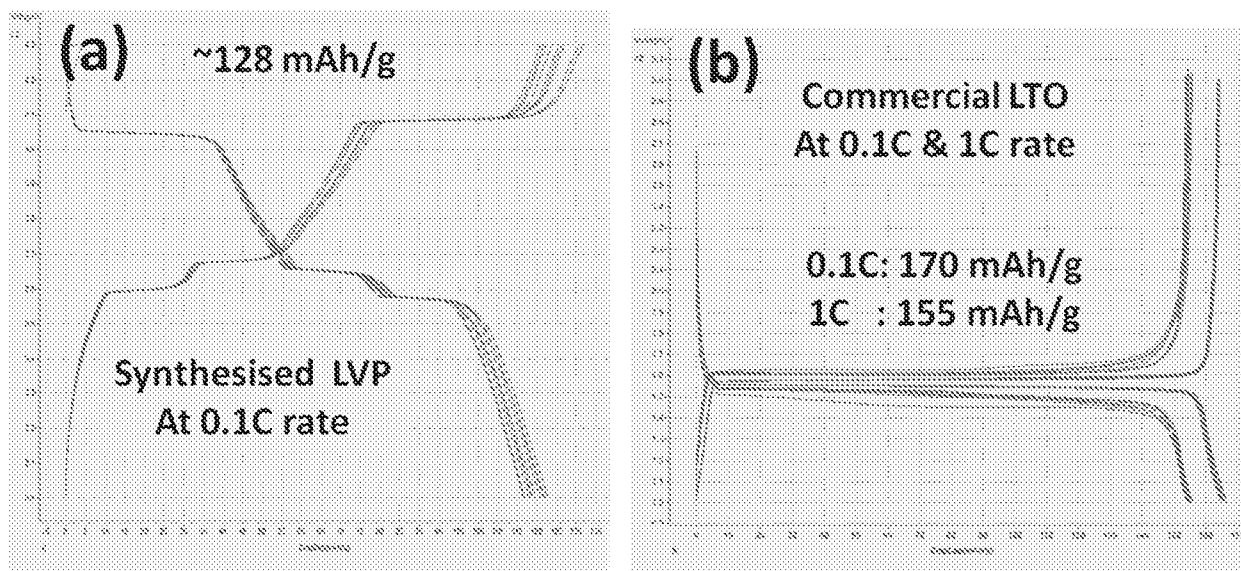


FIG. 11.

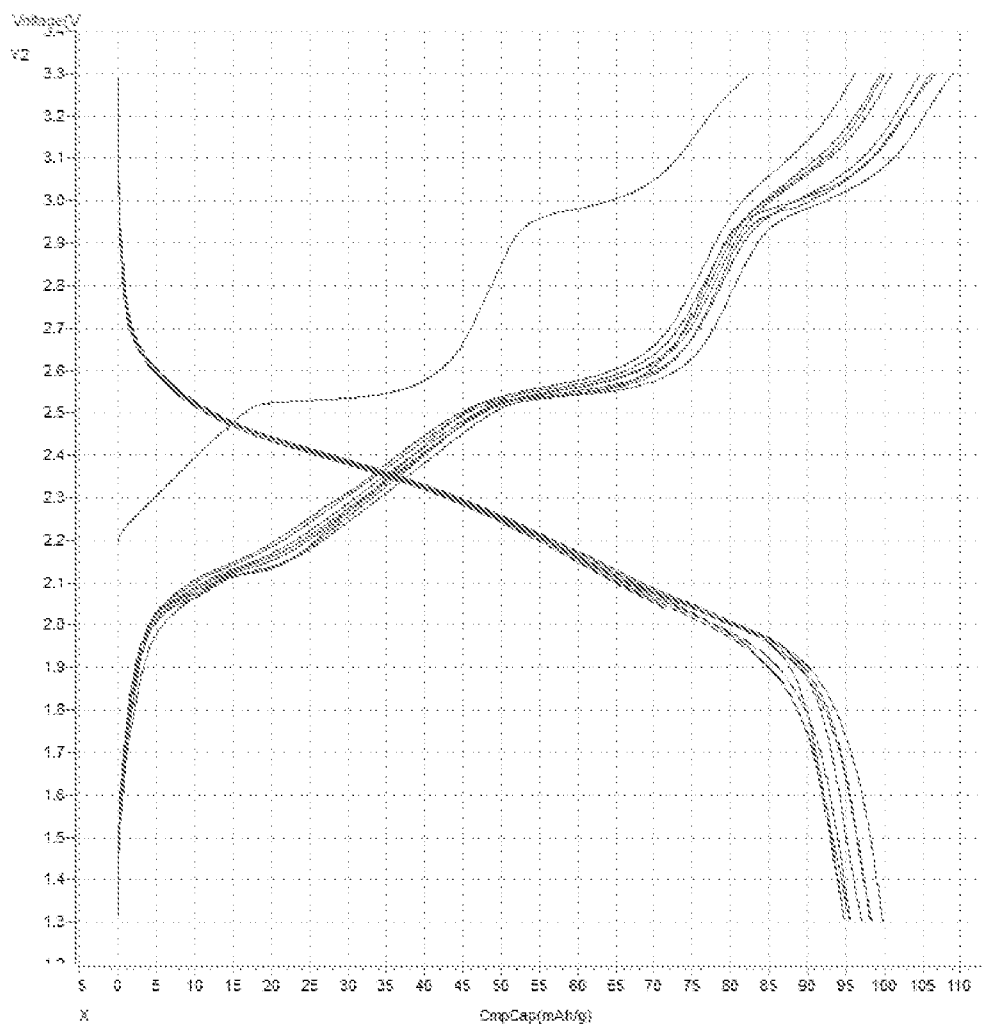


FIG. 12.

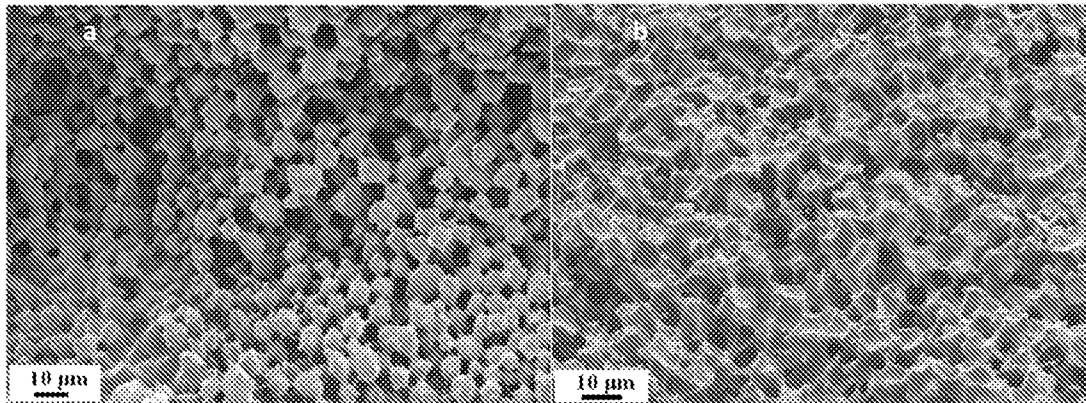


FIG. 13.

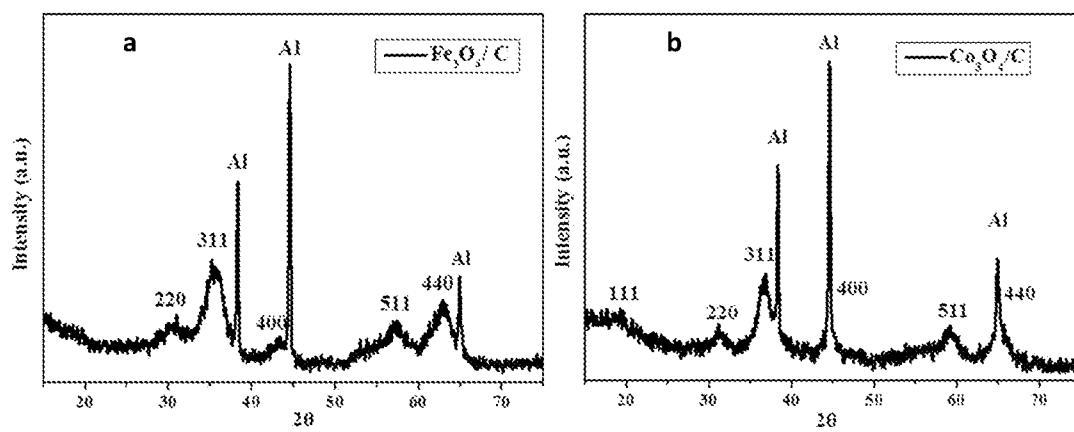


FIG. 14

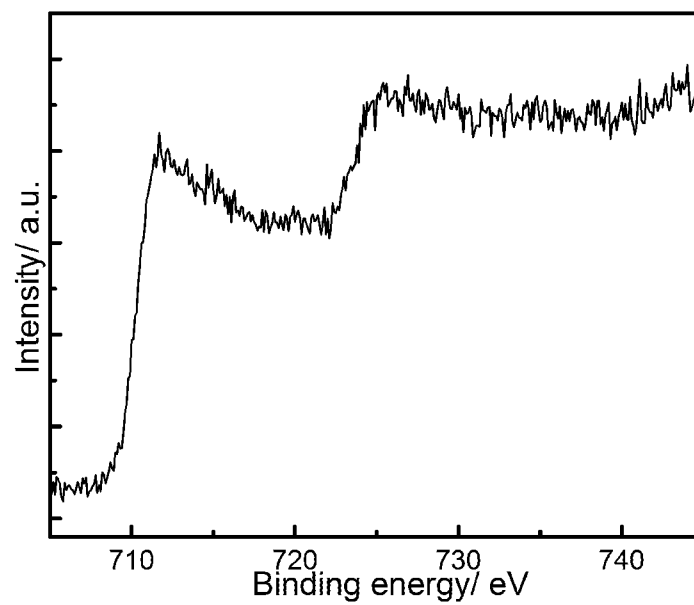


FIG. 15

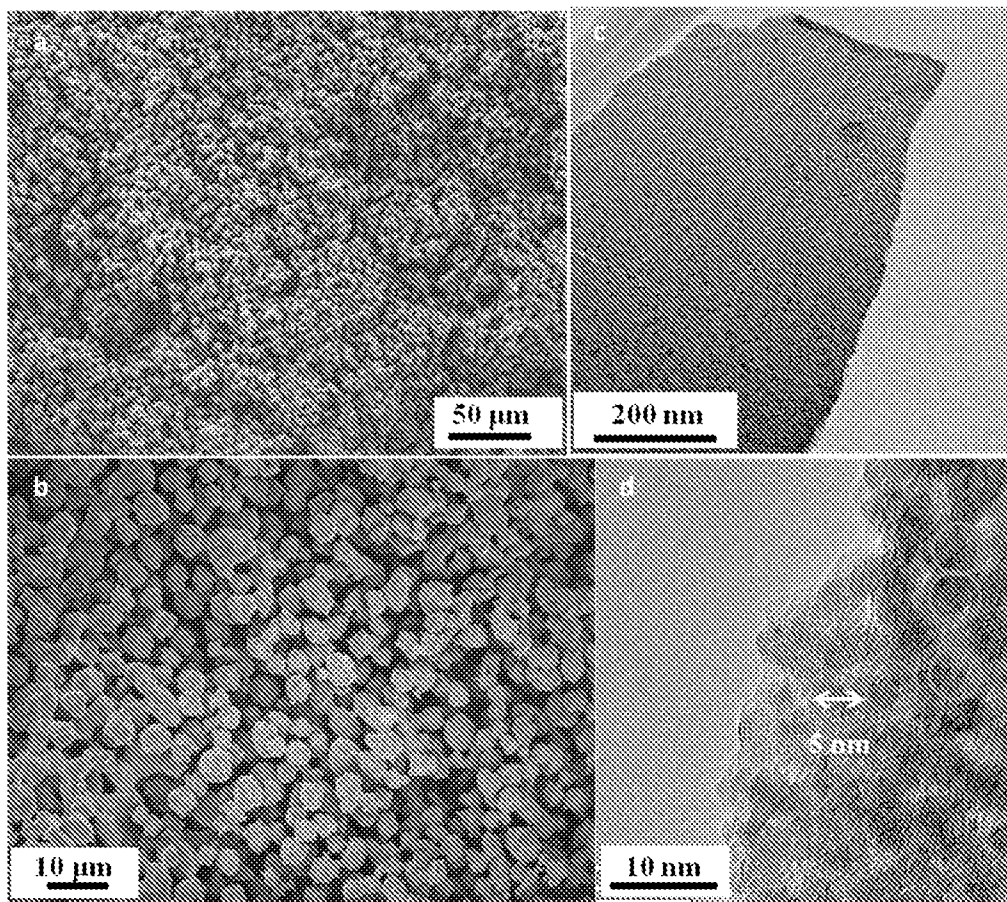


FIG. 16

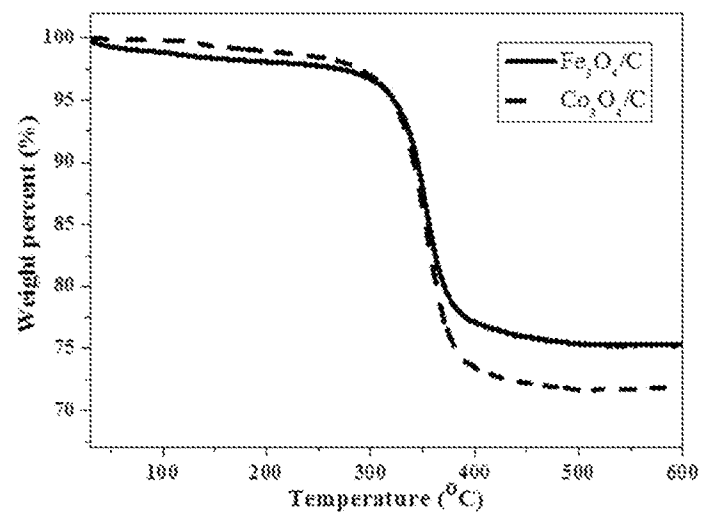


FIG. 17

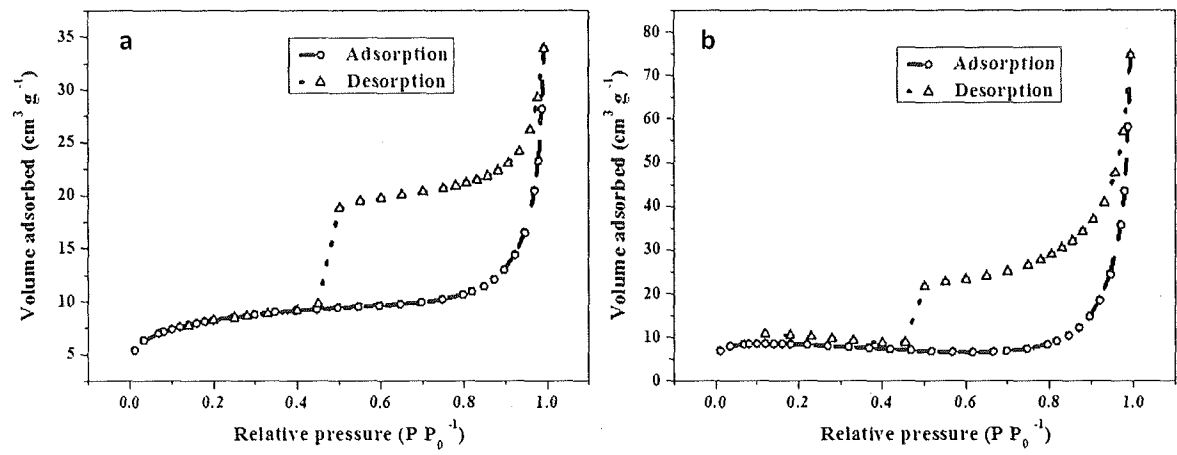


FIG. 18

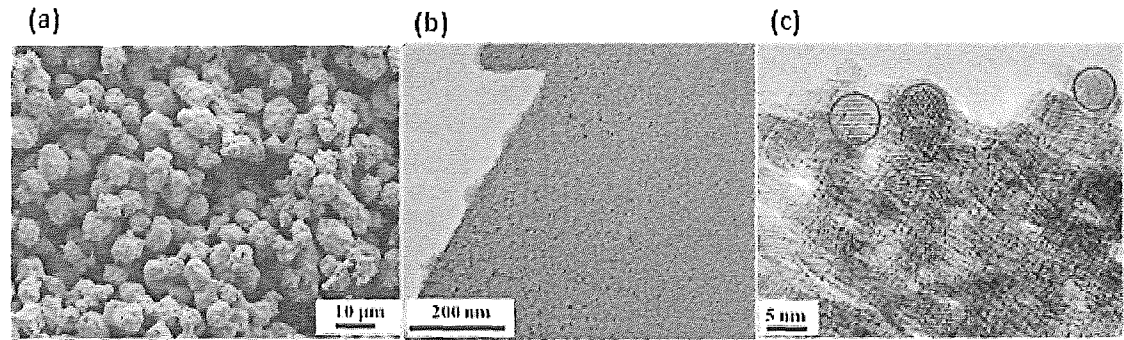


FIG. 19

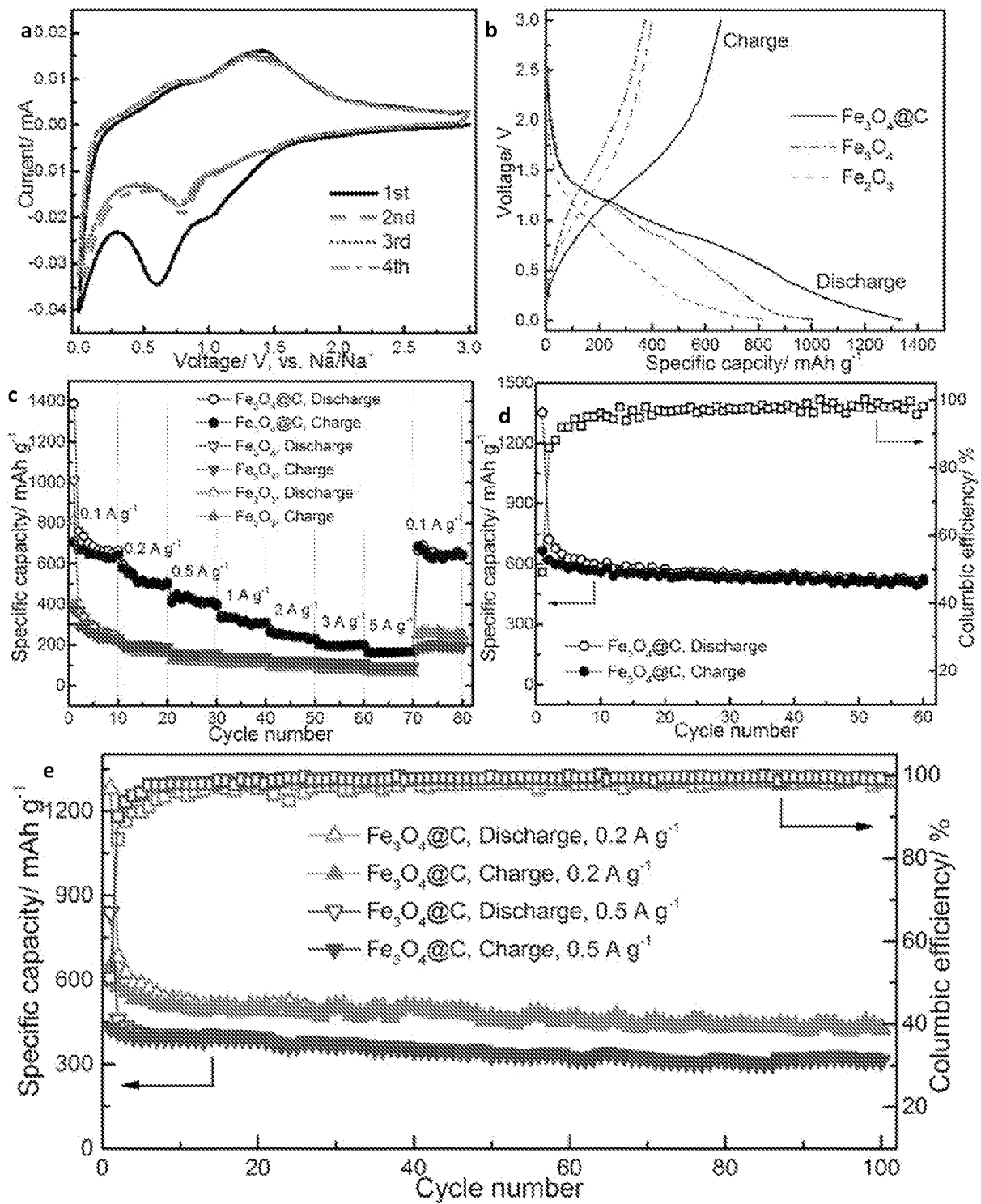


FIG. 20

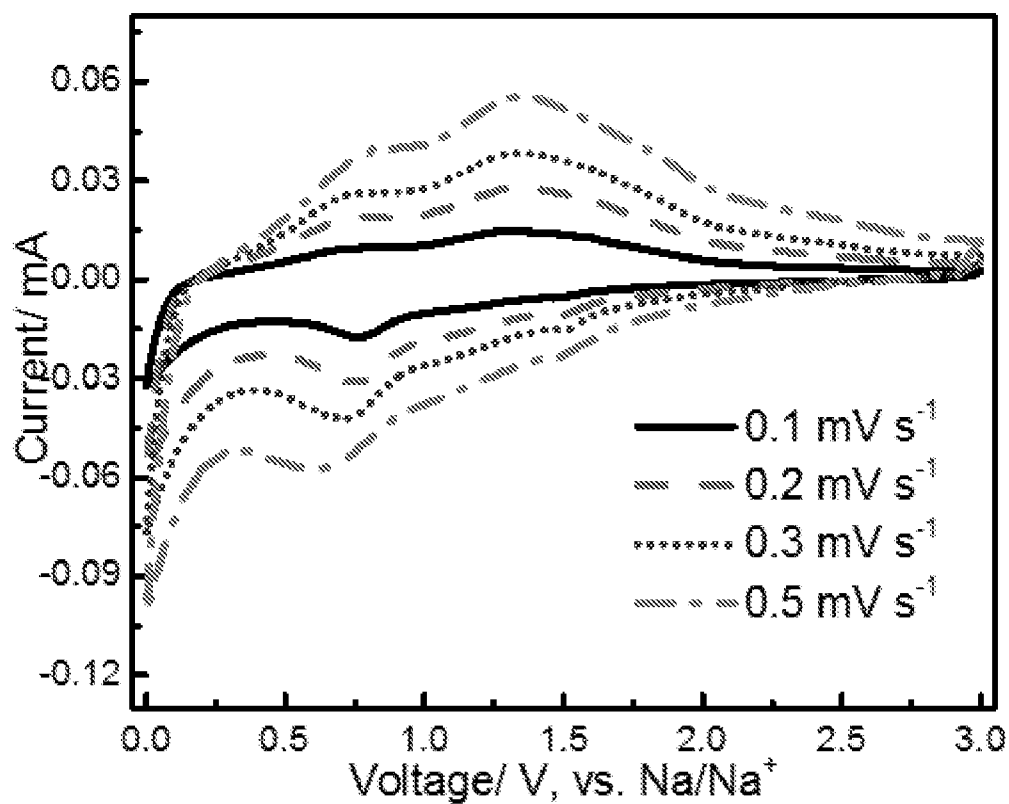


FIG. 21

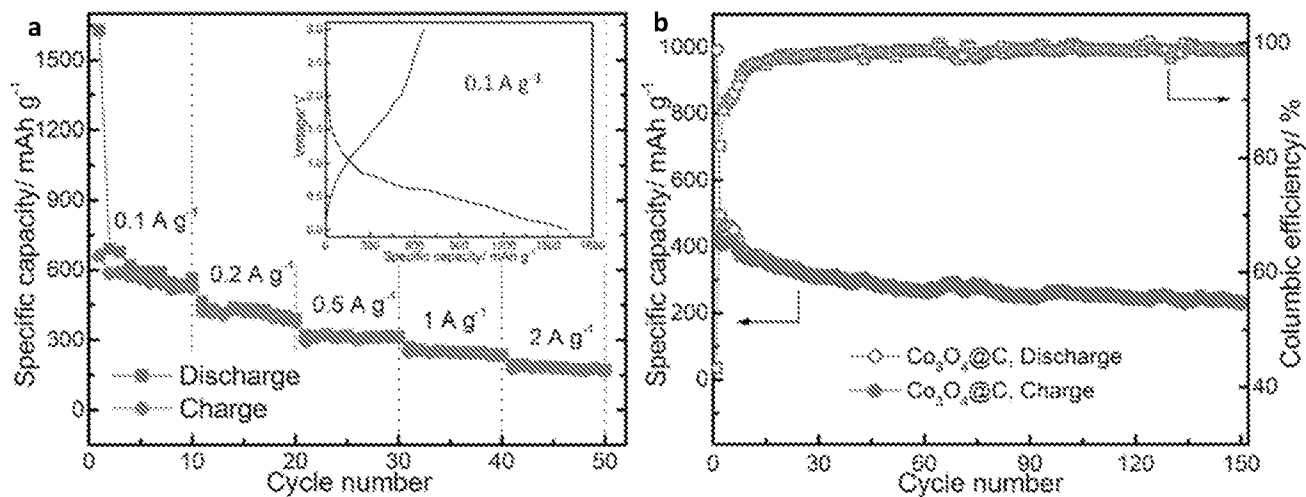


FIG. 22

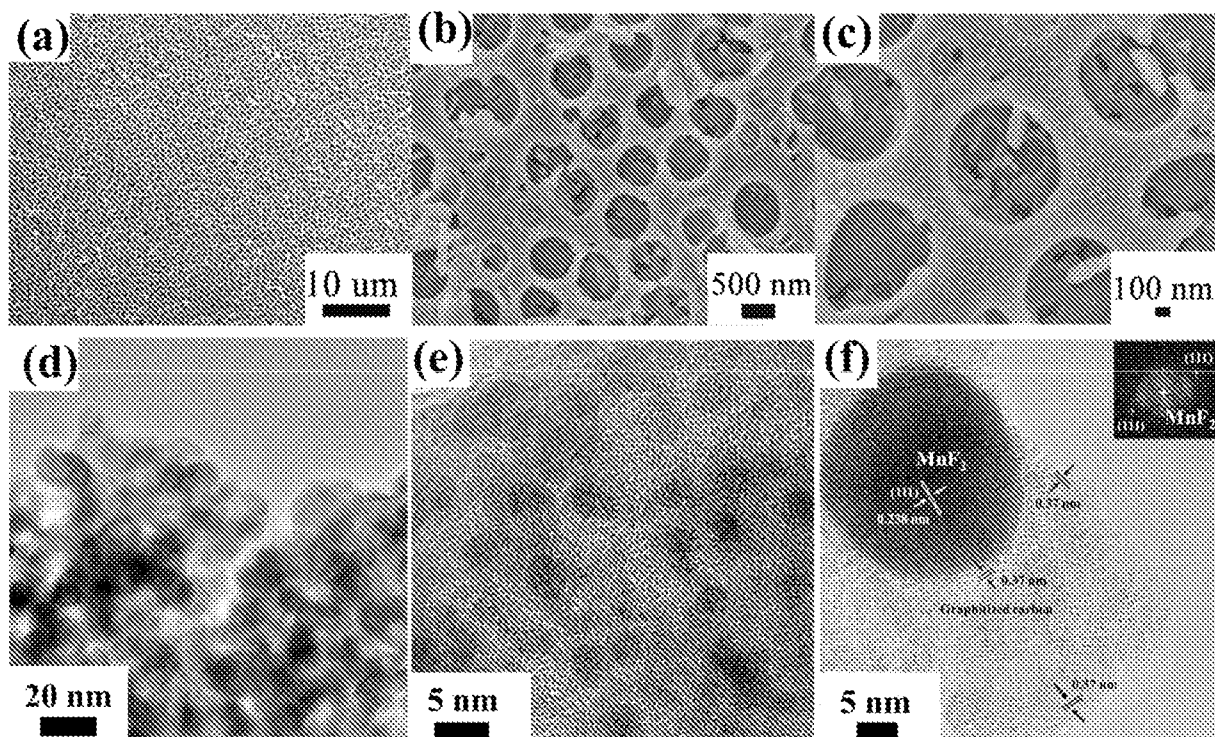


FIG. 23

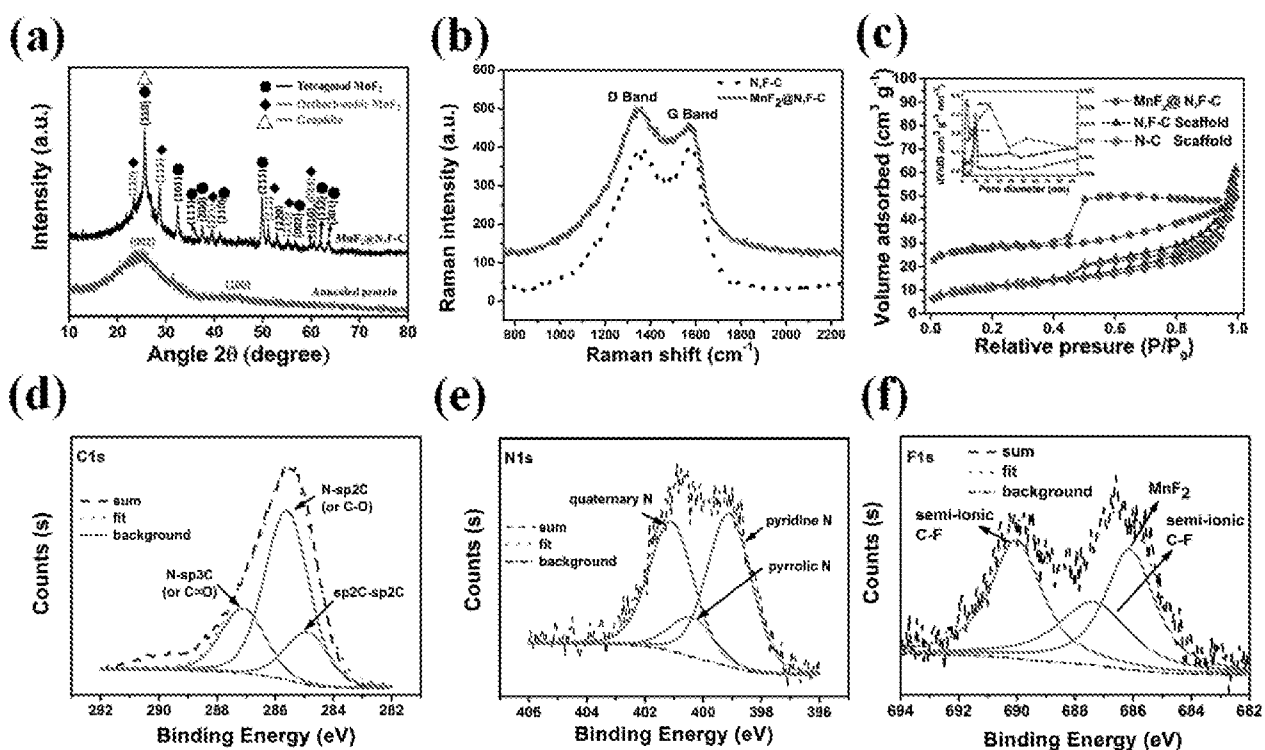


FIG. 24

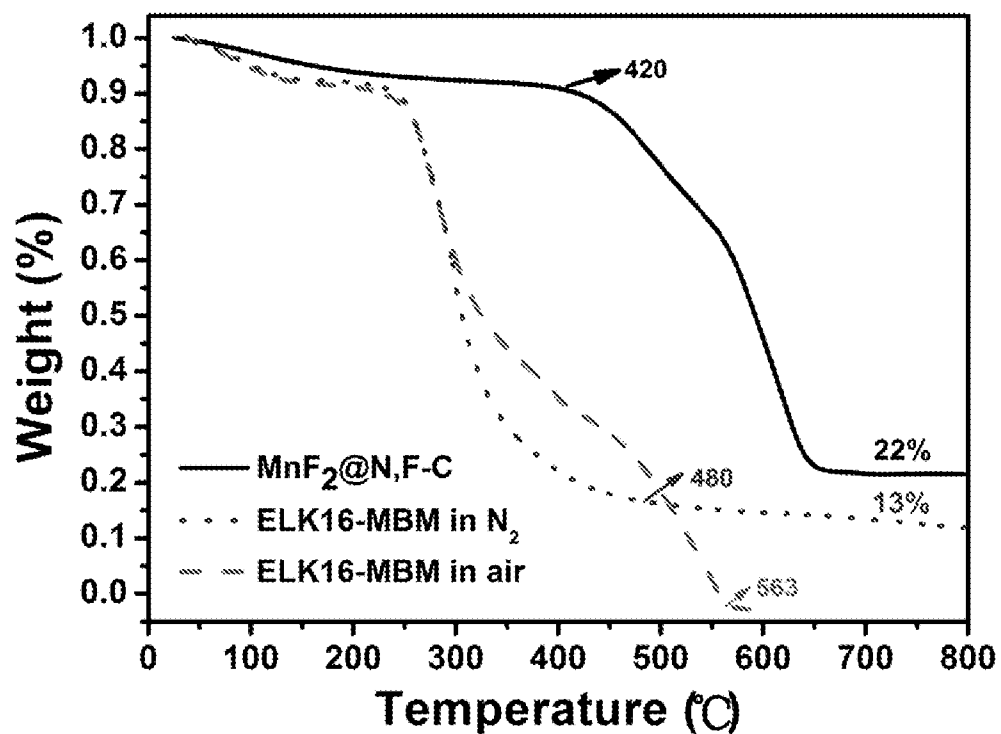


FIG. 25

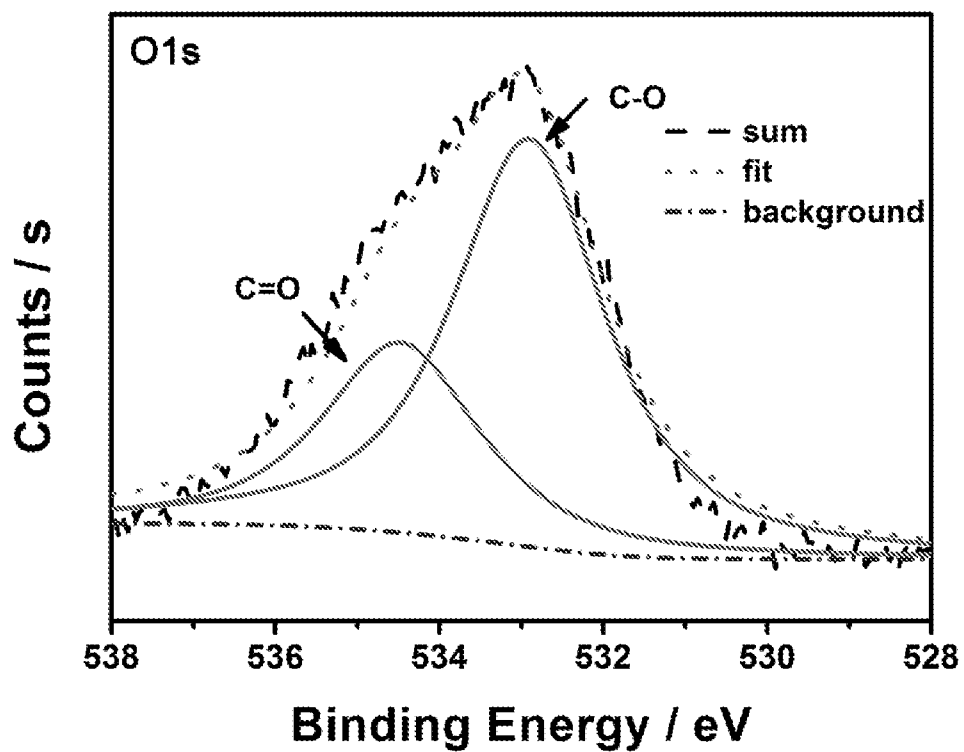


FIG. 26

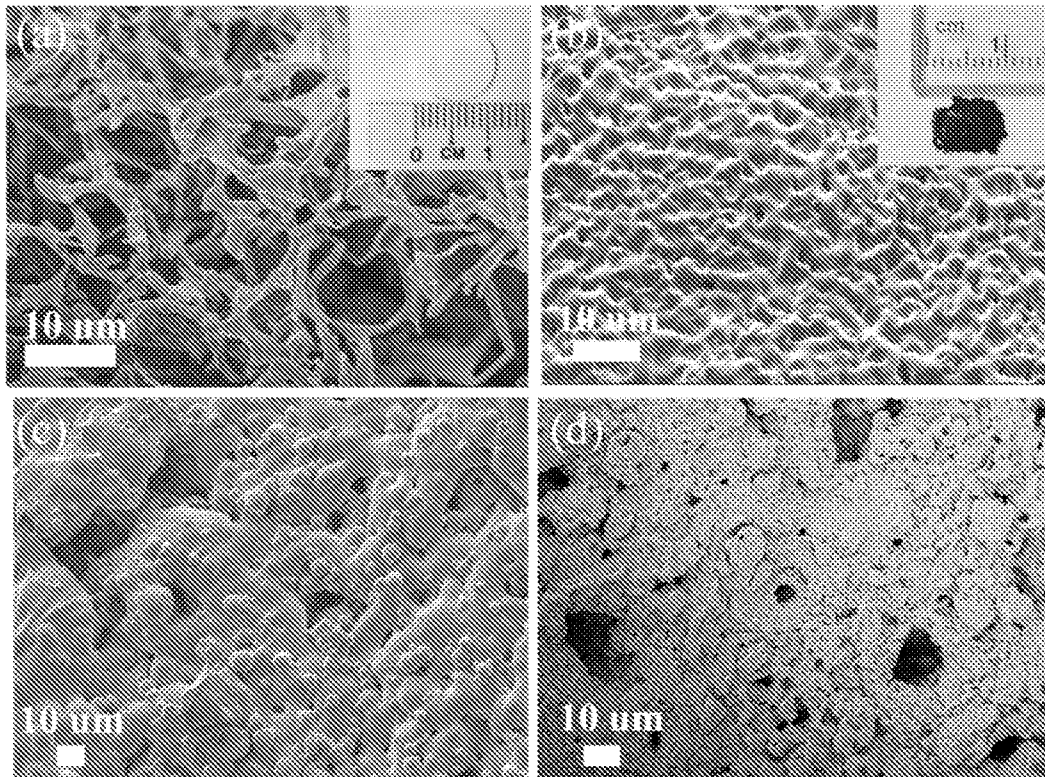


FIG. 27

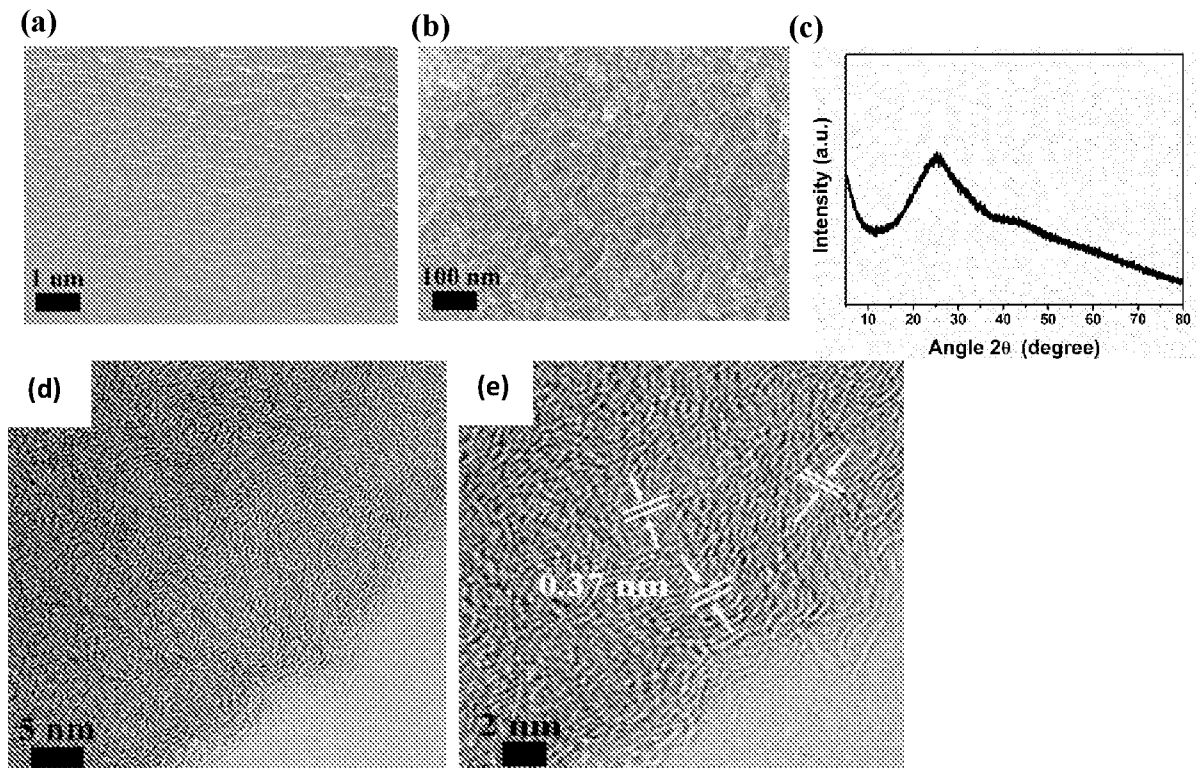


FIG. 28

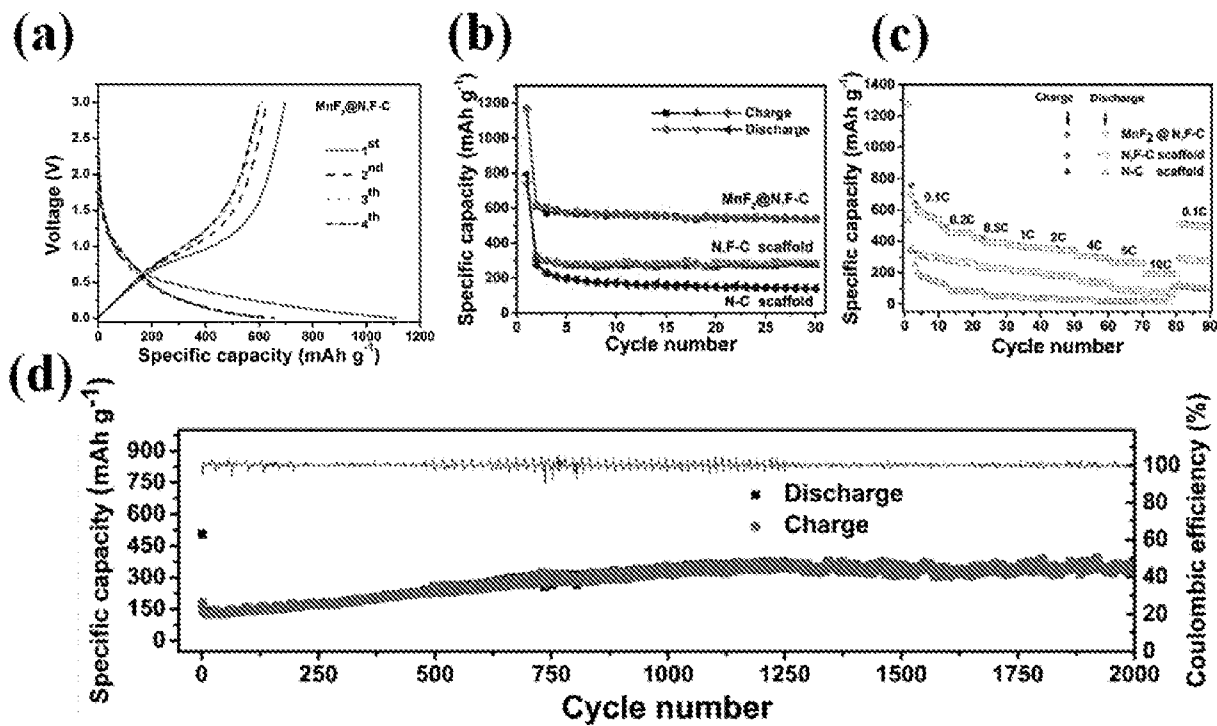


FIG. 29

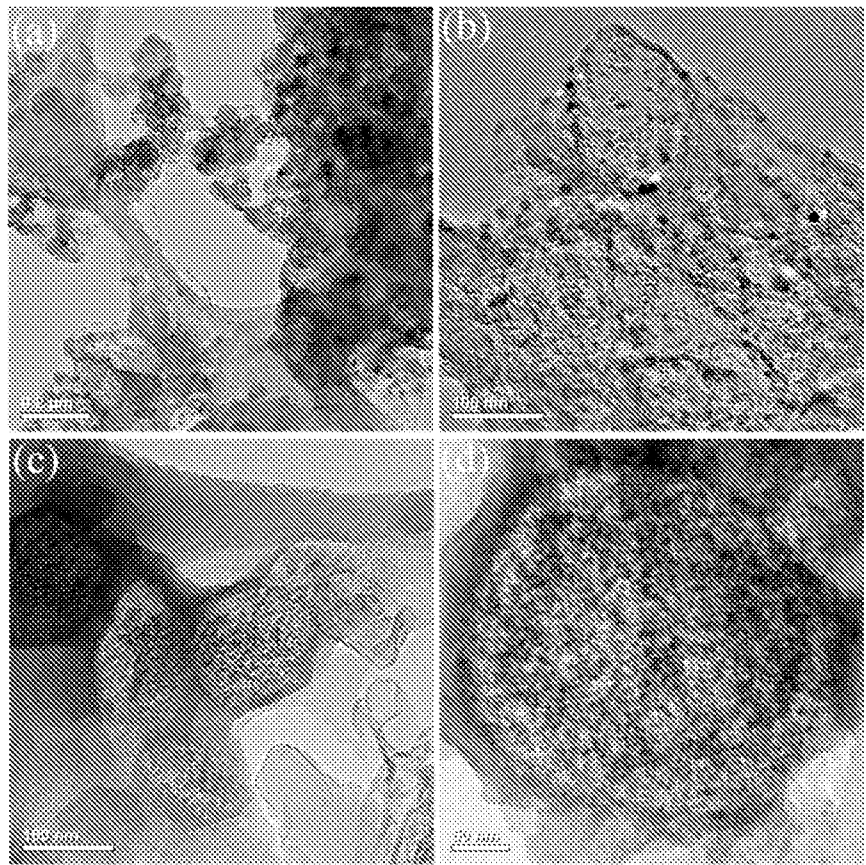


FIG. 30

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M, B82Y, C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

FAMPAT, EPODOC, WPI, SCOPUS, CNKI, STN: phosphate, phosphorous, phosphide, PO₄, carbon, graphite, graphene, skeleton, foam, network, frame, structure, iron, nickel, manganese, cobalt, vanadium, peptide, protein, bio, polymer, assemble, amorphous, porous, coat, layer, encapsulate, cover, embedded, battery, electrode, anode, positive, 蛋白质, 缩氨酸, 电极, 电池, 碳骨架 and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LUO Y., ET AL., Hierarchical Carbon Decorated Li ₃ V ₂ (PO ₄) ₃ as a Bicontinuous Cathode with High-Rate Capability and Broad Temperature Adaptability. <i>Advanced Energy Material</i> , 3 June 2014, Vol. 4, No. 16, pages 1400107:1-8 [Retrieved on 2016-06-20] <DOI: 10.1002/AENM.201400107> Whole document, especially abstract, figs. 1, 3 and 5, p.1, right column, 3 rd para., p.3, left col, 1 st para. p.5, left col, 2 nd para., Supporting Information figs. S2-3	1-6, 15-17
X	CN 102569801 A (JIANGSU YUANJING LITHIUM POWER INDUSTRY CO LTD) 11 July 2012 Whole document, especially claims 1-3, fig. 1, para. [0002], [0004], [0014]-[0016]	1, 3, 15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20/06/2016

(day/month/year)

Date of mailing of the international search report

29/06/2016

(day/month/year)

Name and mailing address of the ISA/SG

Intellectual Property Office of Singapore
51 Bras Basah Road
#01-01 Manulife Centre
Singapore 189554

Email: pct@ipos.gov.sg

Authorized officer

Chen Jiahe (Dr)

IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHANG Q., ET AL. Controllable Construction of 3D-SkeletonCarbon Coated Na ₃ V ₂ (PO ₄) ₃ for High Performance Sodium Ion Battery Cathode. 15 March 2014 [Retrieved on 2016-06-20 from http://ma.ecsdl.org/content/MA2014-03/2/224.abstract] Whole document, especially left col. 2 nd para.	1-6, 15-17
X	RYU J. ET AL., Mineralization of Self-assembled Peptide Nanofibers for Rechargeable Lithium Ion Batteries. <i>Advanced Materials</i> , 26 July 2010, Vol. 22, No. 48, pages 5537-5541 [Retrieved on 2016-06-20] <DOI: 10.1002/ADMA.201000669> Whole document, especially p.5537, right col. 2 nd para; fig.1 (a); p.5540, left col. 1 st para.	1-17
A	NIREESHA G. R. ET AL., Lyophilization/Freeze Drying - An Review. <i>INTERNATIONAL JOURNAL OF NOVEL TRENDS IN PHARMACEUTICAL SCIENCES</i> , 30 October 2013, Vol. 3, No. 4, pages 87-98 [Retrieved on 2016-06-20] <DOI: NOT AVAILABLE> Whole document, especially fig.3	7-14
A	KANG K. ET AL., Bio-Inspired Synthesis of Electrode Materials for Lithium Rechargeable Batteries. <i>Energy Storage in the Emerging Era of Smart Grids</i> , 22 September 2011, Chapter 10 [Retrieved on 2016-06-20] <DOI: 10.5772/18663> Whole document, especially section 2, 1 st and 2 nd para., section 3, 1 st para.	7-14
A	GUO G. ET AL., Platinum and Palladium Nanotubes Based on Genetically Engineered Elastin-Mimetic Fusion Protein-Fiber Templates: Synthesis and Application in Lithium-O ₂ Batteries. <i>Chem Asian J.</i> , 24 June 2014, Vol. 9, No. 9, pages 2555-2559 [Retrieved on 2016-06-20] <DOI: 10.1002/ASIA.201402191> Abstract	7-14
A	ZHU C. ET. AL., Carbon-Coated Na ₃ V ₂ (PO ₄) ₃ Embedded in Porous Carbon Matrix: An Ultrafast Na-Storage Cathode with the Potential of Outperforming Li Cathodes. <i>Nano Letters</i> , 28 March 2014, Vol. 14, No. 4, pages 2175-2180 [Retrieved on 2016-06-20] <DOI: 10.1021/NL500548A> Abstract	1-17
P,X	ZHANG Q. ET AL., Controllable construction of 3D-skeleton-carbon coated Na ₃ V ₂ (PO ₄) ₃ for high-performance sodium ion battery cathode. <i>Nano Energy</i> , 18 December 2015, Vol. 20, pages 11-19 [Retrieved on 2016-06-20] <DOI: 10.1016/J.NANOEN.2015.12.005> Abstract	1-6, 15-17
P,X	ZHOU Y. ET AL., Biochemistry-Enabled 3D Foams for Ultrafast Battery Cathodes. <i>ACS Nano</i> , 15 April 2015, Vol. 9, No. 4, pages 4628-4635 [Retrieved on 2016-06-20] <DOI: 10.1021/ACSNANO.5B00932> Abstract	1-17

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

Box No. I Nucleotide and/or amino acid sequence(s) (Continuation of item 1.c of the first sheet)

1. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of a sequence listing:
 - a. ☐ forming part of the international application as filed:
 - ☐ in the form of an Annex C/ST.25 text file.
 - ☐ on paper or in the form of an image file.
 - b. ☐ furnished together with the international application under PCT Rule 13~~ter~~.1(a) for the purposes of international search only in the form of an Annex C/ST.25 text file.
 - c. ☐ furnished subsequent to the international filing date for the purposes of international search only:
 - ☐ in the form of an Annex C/ST.25 text file (Rule 13~~ter~~.1(a)).
 - ☐ on paper or in the form of an image file (Rule 13~~ter~~.1(b) and Administrative Instructions, Section 713).
2. ☐ In addition, in the case that more than one version or copy of a sequence listing has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

3. Additional comments:

Although a sequence listing has been filed or furnished, it was not used for the purposes of this search.

Since only one version or copy of a sequence listing has been filed or furnished, the statements under item 2 are not required.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:

because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:

because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please refer to Supplemental Box (Continuation of Box No. III).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-17

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

Supplemental Box

(Classification of Subject Matter)

Int. Cl.

H01M 4/36 (2006.01)

H01M 4/04 (2006.01)

B82Y 40/00 (2011.01)

C07K 14/00 (2006.01)

H01M 4/02 (2006.01)

C01B 25/30 (2006.01)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2016/050151

Supplemental Box (Continuation of Box No. III)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-17: a composite material having nanocrystalline mixed-metal phosphate or a method for preparing the corresponding composite material or a cathode comprising the corresponding composite material;

Claims 18-32: a composite material having nanoparticles of a metal oxide or a method for preparing the corresponding composite material or an anode comprising the corresponding composite material;

Claims 33-48: a composite material having a nanocrystalline metal fluoride or a method for preparing the corresponding composite material or an anode comprising the corresponding composite material;

Please refer to **Box No. IV** of Written Opinion of The International Searching Authority (Form PCT/ISA/237) for detailed explanation.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2016/050151

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 102569801 (A)	11/07/2012	NONE	