Unveiling of the energy storage mechanisms of multi -modified (Nb₂O₅@C)/rGO nanoarrays as anode for high voltage supercapacitors with formulated ionic liquid electrolytes

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ABSTRACT

A better understanding of the energy-storage mechanisms in complex pseudocapacitive nanostructures is essential to improve the performances of nanohybrid supercapacitors. In this study, highly interface modified Nb₂O₅ nanoarrays, attached to graphene nanosheets, were carefully designed and synthesized. The electrochemical performances were evaluated in an organic electrolyte, a formulated ionic-liquid mixture electrolyte, and a nanocomposite ionogel electrolyte, respectively. The capacitive and faradaic storage contributions were assessed qualitatively in diverse electrolytes at various temperatures. The capacitive contribution in the ionic liquid electrolyte was found to rise with increasing temperature. A molecular dynamics simulation proved that the increased diffusion coefficient of large ions was much more pronounced than that of the small Li⁺ ions. A carefully optimized quasi-solid-state lithium ion capacitor, fabricated using a (Nb₂O₅@C)/rGO nanoarchitecture as the anode and an ionic liquid gel separator, delivered an energy density of 101 Wh kg⁻¹ and a power density of 24 kW kg⁻¹ at 60 °C. The efficient coupling between the nanohybrids and a complex ionogel electrolyte opens a new window for the rational design of high energy-density supercapacitors.

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1. Introduction

There is an urgent need for advanced energy-storage devices that can satisfy the fast growing demand for high-energy, high-power, and low-cost energy-storage systems [1–4]. Lithium ion capacitors (LIC), a promising new hybrid storage device, combine the high power density of supercapacitors (SCs) with the high energy density of lithium ion batteries (LIBs) [5–8]. They have broad potential applications in hybrid electric vehicles, public transportation, and smart grids. Generally, LICs consist of faradaic-type anodes and capacitive-type porous-carbon cathodes. Such a configuration can effectively couple the merits of LIBs and SCs

[9,10]. However, the performances of LICs are heavily dependent on the anode materials, which may cause sluggish redox reactions. Therefore, sufficient efforts have been made to improve the design and optimization of advanced high-power anodes for the sake of balancing the kinetics between the anodes and cathodes [11,12].

An effective way to improve the kinetics and capacity of anodes is to introduce carefully designed hybridized nanoarchitectures [13,14]. Orthorhombic niobium pentoxide (T-Nb₂O₅) is regarded as the most satisfactory candidate [15,16]. One Nb₂O₅ unit cell can be transformed into Li₂Nb₂O₅ by inserting two Li⁺ ions, which make it exhibit a remarkable capacity of ~200 mA h g⁻¹, superior to conventional high-power materials, e.g., Li₄Ti₅O₁₂ and TiO₂ [17,18]. In addition, Nb₂O₅ can deliver a high rate capacity owing to the capacity-like processes of Li⁺ on the surface and a fast intercalation reaction [19,20]. Previous studies indicated that the fast Li⁺ ion diffusion takes place in two-dimensional tunnels built via the connection of empty octahedral sites between the (001) planes

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[21–24]. Furthermore, the formation of lithium dendrite can be effectively avoided as Nb_2O_5 has a high intercalation potential (1.4–1.8 V vs. Li/Li^+). Such a feature makes Nb_2O_5 safer and work for an ultralong cycle life [25].

Nevertheless, the high rate and practical applications of Nb_2O_5 are hindered by its low intrinsic conductivity ($\sim 3.4 \times 10^{-6} \text{ S cm}^{-1}$ at 300 K) and severe structural deformation that takes place during the Li^+ de/intercalation processes [20,26]. Numerous efforts are being devoted to enhancing the conductivity of the Nb_2O_5 electrode without sacrificing its capacity. So far, modification with nanocarbons and dimension reduction are considered the most effective strategies to overcome the abovementioned issues [27–29]. Carbon nanotubes and graphene are being investigated as conductive additives for the semiconducting Nb_2O_5 . Commonly used nanocarbons include carbon nanotube, graphene, etc. Three-dimensional porous $\text{Nb}_2\text{O}_5/\text{rGO}$ nanocomposite was found to exhibit a high areal capacity and a high rate capability under practical mass loading [17]. A free-standing $\text{Nb}_2\text{O}_5/\text{rGO}$ electrode formed via a facile polyol-mediated solvothermal process was found to exhibit a high capacity reaching 620.5 F g^{-1} [30]. Simply mixing Nb_2O_5 nanocrystals with carbon nanotubes also improves the rate capability [31]. To modulate the microstructures of Nb_2O_5 , various methods have been proposed, such as dimension reduction and optimization of the porosity characteristics. Three-dimensional, hollow hierarchical structures formed via a hydrothermal route exhibited an energy density of 86 Wh kg^{-1} [32]. In another study, three-dimensional ordered mesoporous hierarchical T- Nb_2O_5 synthesized by a hard template procedure delivered a capacity of 106 mA h g^{-1} at 20°C [33]. T- Nb_2O_5 quantum dots embedded in porous carbon demonstrated an excellent cycling performance and a high energy density of 76.9 Wh kg^{-1} [34]. These findings imply that the optimization of the electrodes' microstructures is an effective approach to achieve satisfactory performances. Besides utilizing high specific capacitive electrodes, widening the working potential is another effective approach to attaining high energy-density capacitors. Because of their excellent electrochemical properties, ionic liquids (ILs) can effectively widen the operation window for LICs [35]. Nanocomposite ionogel polymer electrolytes display better electrochemical stability and mechanical strength than normal polymer electrolytes or pure IL. Such promising electrolyte separators generally consist of a polymer scaffold, an IL, and inorganic pillars [36,37]. In addition to their high thermal and electrochemical stability, negligible vapor pressure, and high ionic conductivity, ILs reduce interface resistance and inhibit the growth of lithium dendrites [35,38,39]. The introduction of a few ILs can not only maintain the thermal stability and mechanical strength of the separators, but also reduce their brittleness. The compatibility between rationally designed nanocomposite ionogel electrolytes and nanoarchitected electrodes should be systematically optimized to reveal their full potential [40].

Another challenge to realizing high performance symmetrical solid-state SCs is a comprehensive understanding of the intrinsic energy-storage mechanisms and synergetic effects, which are obscured by their complex configurations [41]. A previous study revealed that the capacitive contributions of TiO_2 nanoparticles become recessive with increasing size [42]. With the help of a carbon shell, the capacitive contribution rose from 83% in pristine Nb_2O_5 to 93% in core-shell $\text{Nb}_2\text{O}_5/\text{C}$ nanoarchitectures; thus, the carbon shell improved both the interface compatibility and the capacitive process [43]. While little studies has been paid to the influence of complex electrolytes, especially formulated IL electrolytes and nanocomposite ionogel polymer electrolytes, on the energy-storage mechanisms of complicated electrode materials.

In this paper, a novel pseudo-capacitive ($\text{Nb}_2\text{O}_5/\text{C}$)/rGO

nanocomposite was synthesized to study its energy-storage mechanisms. Its electrochemical performance was evaluated in three different electrolytes at various temperatures. The capacitive and faradaic contributions were estimated by qualitatively and quantitatively analyzing the CV profiles. To unveil the storage mechanisms in the complex formulated electrolytes, the mobility of different ions was simulated using molecular dynamic methods.

2. Experimental section

2.1. Materials

Ammonium niobate (V) oxalate hydrate ($\text{C}_4\text{H}_4\text{NNbO}_9 \cdot x\text{H}_2\text{O}$, purity $\geq 99.5\%$), hexadecyl trimethyl ammonium bromide (CTAB, purity $\geq 99\%$), natural graphite flakes (325 mesh), acetylene black (ACET), and N-methyl pyrrolidone (NMP) of analytical grade were used. Carbon-coated aluminium foil and carbon-coated copper foil were all purchased from the MTI (Hefei) company, and the carbon mass loading of aluminium foil and copper foil are 1.12% and 1.15%, respectively. Activated carbon (Kuraray YP-50F) was used without further treatment.

Graphene oxide (GO) nanosheets were prepared by exfoliating natural graphite flakes via a modified Hummers' approach [44].

2.2. Synthesis of ($\text{Nb}_2\text{O}_5/\text{C}$)/rGO nanocomposite

The ($\text{Nb}_2\text{O}_5/\text{C}$)/rGO nanocomposite was fabricated in simple two steps: hydrothermal and post-annealing treatments. Under magnetic stirring, 1.176 g of ammonium niobate (V) oxalate hydrate (3.882 mmol) and 2.1 g of CTAB were added into a 60 ml GO suspension (1 mg/mL) to form a uniform solution. Then, the as-formed mixture was transferred into a 100 mL Teflon-lined autoclave and maintained at 170°C for 48 h. After cooling naturally, the black precursors were washed by ultrapure water and freeze dried for further characterizations. The phase transformation to ($\text{Nb}_2\text{O}_5/\text{C}$)/rGO was realized by annealing the as-obtained precursor at an elevated temperature. $\text{Nb}_2\text{O}_5/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{C}$ were synthesized via an identical process, with only GO and CTAB, respectively, as the templates.

2.3. Preparation of ionic-liquid (IL) and ionogel electrolytes

The ionogel separator was prepared by a solution-casting technique. To produce a homogeneous solution, 0.5 g of PVDF-HFP was dissolved into 3.0 g of NMP. Then, 0.5 g of LiTFSI and 0.5 g of EMIMBF₄ were added to generate a highly viscous and homogenous solution. This viscous mixture was cast into a polytetrafluoroethylene model. Finally, a free-standing film with a thickness of $\sim 50 \mu\text{m}$ was obtained after the mixture was dried overnight at 80°C under vacuum. The as-formed P(VDF-HFP)-EMIMBF₄-LiTFSI ionogel separators were stored inside a glove box for further characterizations. The IL electrolyte was prepared by mixed IL and lithium salt. EMIMBF₄ and LiTFSI were mixed by mass ratio 1:1, the IL electrolyte was obtained after the mixture was stirred at 40°C for 1 h.

2.4. Molecular dynamics (MD) simulation

The simulation system was constructed inside a cubic box with 300 Li^+ , 300 TFSI^- , 435 EMIM⁺, and 435 BF_4^- ions, which represented the LiTFSI/EMIMBF₄ electrolyte with a mass ratio of 1:1. All MD simulations were conducted with the Gromacs 5.1.1 package, and a OPLS-AA force field was applied for the Li^+ , TFSI^- , EMIM⁺, and BF_4^- ions [45]. The energy of the whole system was initially minimized over 10,000 steps through the steepest descent method

to remove abnormal contacts among the ions. Then, the system was heated to 400 K, and short MD runs of 5 ns using a 1 fs time step under the NVT (number volume temperature) ensemble were performed. Next, a 5 ns simulation under an NPT (number pressure temperature) ensemble to cool down the system from 400 K to 298 K, 308 K, 318 K, 328 K, and 338 K was run. Finally, a production run of 30 ns with a 2 fs step was performed under the NPT ensemble for the above temperature systems. The particle-mesh Ewald (PME) method was employed to simulate the long-range electrostatic interactions, and the cut off radius was fixed at 1.1 nm for the electrostatic and van der Waals interactions [46]. The temperature was maintained by the V-rescale algorithm and pressure was controlled at 1 bar by the Parrinello-Rahman algorithm [47]. A static electric field was applied to the above temperature systems in the z-direction with a strength of 2.7×10^{-5} V/nm.

2.5. Electrochemical measurements

The anode slurry was obtained by mixing the active compound (80 wt%), acetylene carbon black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) homogeneously in N-methyl-2-pyrrolidone (NMP). Then, the slurry was spread over a carbon-coated copper foil and dried overnight in a vacuum oven at 80 °C. The cathode slurry was obtained by mixing activated carbon, carbon black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%). This mixture was pressed onto a carbon-coated aluminium foil. The mass loading of anode and cathode electrodes was about 1 mg and 1.8 mg. All electrochemical performances were studied using CR2016-type coin cells, which were constructed in an Ar-filled glove box. In addition to the as-prepared ionogel separator, an organic LiPF₆ (1.0 M) (EC: DEC: DMC = 1:1:1, volume ratio) electrolyte and the formulated ionic-liquid mixture (LiTFSI: EMIMBF₄, 1:1) were also used as electrolytes. For the half-cell evaluation, lithium discs were used as both the counter and reference electrodes, and Celgard 2325 porous film was used as the separator. The LICs were assembled utilizing nanohybrids as the anodes and activated carbon as the cathodes. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results were analyzed on a ZAHNER IM6 workstation with a frequency range of 0.01–100 KHz. Galvanostatic charge–discharge (GCD) behaviors were evaluated using a LAND battery test system (CT2001A).

3. Results and discussion

3.1. Synthesis and properties of Nb₂O₅ nanoarray material

The morphologies and microstructures of the as-obtained nanoarchitectures were investigated via electron microscopy. In one representative sample, shown in Fig. 1a, grass-like Nb₂O₅ nanorods were attached to some flat plates on both sides of the nanoarrays. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) investigation (Fig. 1b) revealed that these nanorods had cone-shape tops with relatively sharp tips and an average diameter of 40 nm. It is clear that the contrast of the nanorod images was not uniform, suggesting a porous structure and that they may be composed of smaller nanoparticles. The high-resolution scanning transmission electron microscopy (HRSTEM) analysis (Fig. 1c) confirmed that these nanorods had porous features and were composed of many connected, irregular nanoparticles. These nanoparticles had a broad size distribution of 5–12 nm. Numerous gaps and tunnels were formed, and the agglomeration of the smaller nanoparticles was slight. Such a behaviour may be caused by the absorbed CTA⁺ chains, e.g., the formed amorphous nanocarbon might prevent the direct contact of neighbouring nanoparticles. These gaps and

porous channels might also facilitate the rapid transport of ions. The smaller nanoparticles were highly crystallized and had obvious lattice fringes (Fig. 1d). The lattice fringe widths of 0.39 nm and 0.31 nm were ascribed to the (001) and (200) planes, respectively, of the orthorhombic Nb₂O₅. Many obvious grain boundaries existed among neighbouring nanocrystals. A grain boundary was formed in the (201) plane, highlighted by a dashed rectangle (Fig. 1d), to reduce the total surface energy. A bright-field high-resolution TEM (HRTEM) analysis (Fig. S1) was conducted to prove the formation of amorphous carbon on the surface of the Nb₂O₅ nanoarrays. The unclear lattice fringes of the nanorods, highlighted by circles in Fig. S1, could be caused by the amorphous carbon formed via the carbonation of CTAB. Moreover, as shown by the energy-dispersive X-ray spectroscopy (EDX) elemental mapping analysis (Fig. 1e), it is apparent that the elements of (Nb₂O₅@C)/rGO, i.e., niobium, oxygen, and carbon, were uniformly distributed.

Based on the above microstructure analysis, a four-step procedure (Scheme 1) was proposed for the formation of desired (Nb₂O₅@C)/rGO nanoarchitectures. Firstly, negatively charged graphene oxide (GO) nanosheets were mixed with the templating agent CTAB and a niobium precursor, as illustrated in step I. These positively charged Nb⁵⁺ and CTA⁺ cations naturally attached themselves to the negatively charged GO nanosheets by electrostatic interaction. Most importantly, the positively charged ions became concentrated around the positively charged defects. With the help of OH[−] ions released via the hydrolysis of ammonium niobate (V) oxalate hydrate, the crystal nucleus of the Nb₂O₅ precursor formed firstly in the concentrated Nb⁵⁺ regions, and became surrounded by CTA⁺ in a hydrothermal environment (step II). Generally, surfactant molecules tend to organize spontaneously into rod-shape micelles once their concentration surpasses a critical value [48]. As a result, the anisotropic growth of the Nb₂O₅ nanoarrays was realized due to the confinement effect from the one-dimensional CTA⁺ micelles (step III). Such a process can be explained by a templating against self-assembled theory [49]. Undoubtedly, uniform rods would form if sufficient reaction intermediates were supplied during the growth stage. The formation of a cone terminal, as illustrated in step III, during the later growth stage was caused by the gradually declining concentration of the Nb⁵⁺ precursor. Finally, the transformation of Nb₂O₅ from the amorphous phase to the orthorhombic crystallographic phase and the formation of amorphous carbon via the carbonation of CTA⁺ ions were achieved by annealing at 600 °C in flowing Ar (step IV).

X-ray diffraction (XRD) patterns were collected to monitor the crystallographic transformation process and to assess the effects of utilized templates, both soft CTAB and hard GO nanosheets, on the nucleation (Fig. 2). Three kinds of samples, Nb₂O₅/rGO, Nb₂O₅@C and (Nb₂O₅@C)/rGO, were prepared using GO nanosheets, CTAB, and both GO nanosheets and CTAB as templates, respectively, to tune the nucleation and growth stages. All precursors were obtained by the hydrothermal procedure, the only difference being the type of template used. The only weak peaks observed were at about 22.5 and 45.9° (2θ). Once annealed at 600 °C, all the precursors were transformed into highly crystalline phases, which had analogous XRD diffraction peaks. These diffraction peaks, positioned at 22.5, 28.4, 36.6, 45.9, and 50.5° (2θ), were indexed as the (001), (100), (101), (002), and (102) planes, respectively, of orthorhombic Nb₂O₅ (JCPDS No. 30-0873). Interestingly, the crystal sizes were highly dependent on the templates. The full width at half maximum (FWHM) of the sample obtained in the presence of exfoliated GO nanosheets was broader than that of the sample obtained using CTAB as the template. This indicates that the numerous defects in the GO nanosheets played a large role in the nucleation of the precursor. The FWHM of (Nb₂O₅@C)/rGO was even broader, implying that the combination of the CTAB and GO

Fig. 1. Microstructure characterizations of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrids: a) SEM; b) HAADF-STEM; c,d) HRSTEM images; and e) EDX elemental mapping of C-K α , O-K α , and Nb-K α .

Scheme 1. Schematic illustration of the procedure for fabricating $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanoarrays.

nanosheets favoured the formation smaller particles, as all of them acted as templates. The particle sizes of $\text{Nb}_2\text{O}_5/\text{rGO}$, $\text{Nb}_2\text{O}_5@\text{C}$, and $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ were calculated according to the Scherrer equation

Fig. 2. XRD patterns of a) the as-formed precursor; b) $\text{Nb}_2\text{O}_5@\text{C}$; c) $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$; and d) $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrids.

as 21, 15, and 12 nm, respectively. The value of 12 nm for the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrid matched well with the HRTEM observations (Fig. 1c), and also confirmed that the nanorods were

composed of small nanocrystals.

The state of the nanocarbon was analyzed by reviewing the Raman spectra (Fig. 3a). Both the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrids displayed two obvious peaks located at 1600 cm^{-1} (G-band) and 1350 cm^{-1} (D-band), which should originate from the vibration of sp^2 -bonded carbon atoms in a two-dimensional hexagonal lattice and disordered carbons with defects, respectively. The disorder degree of the carbon can be expressed by the ratio of the intensity of D-band (I_D) to the G-band (I_G), i.e., I_D/I_G . For the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ samples, I_D/I_G was 1.02 and 0.94, respectively. The increased disorder degree in $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ was ascribed to the amorphous nanocarbon formed by the carbonation of adsorbed CTA^+ molecule chains. Another weak peak, positioned at 690 cm^{-1} , was ascribed to the characteristic peak of Nb_2O_5 [43].

X-ray photoelectron spectroscopy (XPS) was utilized to elucidate the chemical environment of the as-fabricated $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrids. The high-resolution C1s core level of $\text{Nb}_2\text{O}_5/\text{rGO}$ (Fig. 3b) was deconvoluted into five peaks, which were positioned at 284.6, 285.4, 286.6, 287.7, and 290.1 eV. They were classified as carbon atoms from the non-oxygenated ring, C-OH, C-O, the carbonyl (C=O), and the carboxylate (O-C=O), respectively [50]. Such a spectrum is analogous to that of hydrothermally reduced GO, indicating the successful reduction of the GO nanosheets upon thermal treatment [51]. Compared with the XPS spectrum of $\text{Nb}_2\text{O}_5/\text{rGO}$, the spectrum of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ displayed an additional peak at 285.1 eV, which is generally ascribed to

disordered carbon. It confirmed the formation of amorphous nanocarbon via the decomposition of the CTA molecule chains. The Nb 3d spectrum (Fig. S2) was resolved into two peaks, positioned at 207.9 eV and 210.7 eV, corresponding to Nb 3d_{5/2} and Nb 3d_{3/2}, respectively [52]. These results reveal the reduction of GO and the formation of Nb_2O_5 .

The carbon content was evaluated by TGA method. Both curves (Fig. 3c) of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ samples display a weak weight loss below 200°C and a pronounced weight loss over 500°C , which correspond to the loss of adsorbed species and carbon decomposition, respectively. Therefore, the nanocarbon contents of each were calculated to be 11.08% and 5.26%, respectively, implying that amorphous nanocarbon was produced via the decomposition of the CTA^+ cation chains. The weight ratio of rGO in the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrid was about 5.8%.

The porosity of the nanohybrids was assessed to determine whether they are suitable for use as anodes. All the nitrogen adsorption/desorption isotherms (Fig. 3d) were type-IV and had adsorption hysteresis loops [53]. The $\text{Nb}_2\text{O}_5/\text{rGO}$ sample displayed a type-H3 hysteresis loop, indicating that the rGO nanosheets induced many slit-shaped pores. The hysteresis loop of $\text{Nb}_2\text{O}_5@\text{C}$ was a combination of type-H2 and type-H4 loops, suggesting that a porous network composed of slit-like pores was also produced by CTAB. In contrast, the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrid exhibited a type-H2 loop. It suggests that a lot of pore necks existed in $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrid [53]. Moreover, the Brunauer–Emmett–Teller

Fig. 3. a) Raman spectra; b) XPS spectra; and c) TGA curves of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrids; and d) nitrogen adsorption/desorption isotherms of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$, $\text{Nb}_2\text{O}_5/\text{rGO}$, and $\text{Nb}_2\text{O}_5@\text{C}$ nanohybrids.

(BET) specific surface areas of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$, $\text{Nb}_2\text{O}_5@\text{C}$, and the $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrid were calculated to be 118.6, 58.5, and $101.4 \text{ m}^2/\text{g}$, respectively. The pore diameter distribution (Fig. S3) confirmed that the average pore width of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ was 81.1 nm, indicating a mesoporous material. Therefore, our sample can provide abundant electrochemical active sites and ion transport tunnels.

3.2. Half cell electrochemical properties

The cyclic voltammetry (CV) curves (Fig. 4a) of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ were collected to check its feasibility as electrode. Nb_2O_5 is a promising intercalation pseudocapacitive material in non-aqueous Li^+ electrolyte because of the rapid Li^+ insertion reaction $\text{Nb}_2\text{O}_5 + x\text{Li}^+ + xe^- = \text{Li}_x\text{Nb}_2\text{O}_5$, $0 < x < 2$ [54]. These CV curves exhibited broad cathodic and anodic peaks between 1.1 and 2.2 V, which were assigned to the fast insertion of two-dimensional Li^+ into the Nb_2O_5 crystal. Moreover, a slight potential separation was found between the cathodic and anodic peaks at a lower sweep rate. Such a behaviour suggests that the Li^+ insertion/extraction processes were highly reversible and fast, and that the corresponding change in crystal structure was negligible. The galvanostatic charge/discharge (GCD) profiles (Fig. 4b) exhibited a sloped pattern at 1.1–2.2 V, which was consistent with the broad cathodic and anodic peaks in the CV test. The absence of an obvious plateau may have been caused by the nanoscale characteristics of the Nb_2O_5 particles. The electrode's first charging capacity was 261.6 mAh g^{-1} , and its discharging capacity was 221.3 mAh g^{-1} (at 100 mA g^{-1}). No significant change took place in the curves

measured after the first cycle. Generally, an irreversible capacity loss of approximately 20–40% is observed in nanostructured electrode materials [16]. The irreversible capacity loss of the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ electrode in this study was 14.6%, suggesting that $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ would be a successful electrode material.

Cyclability is the most important measure of SC performance. The cycle performance (Fig. 4c) and rate capability (Fig. 4d) of the different nanohybrids were assessed to study the effect of the modified nanocarbons. The initial specific discharge capacities of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ were 221.2 and 219.0 mAh g^{-1} . Their capacities were 189.2 and 133.9 mAh g^{-1} after 100 cycles. It is clear that a $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ electrode could provide a long-term cycling stability of up to 300 cycles while retaining 76.3% of its initial capacity. As to rate performance, there was no significant difference between $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ at a low current density; both samples displayed a specific capacity of around 250 mAh g^{-1} at 0.1 C . The advantages of the modified nanoparticle only became evident at a higher current density. At 5 C , the specific capacities of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ were 143.1 and 94.6 mAh g^{-1} , respectively. Furthermore, the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$'s specific capacity returned to 225 mAh g^{-1} when the current density was reduced back to 0.1 C . The greatly improved rate capability, especially at the high current density, may be caused by the porous structure of the Nb_2O_5 nanoarrays improving the electrolyte penetration and shortening the ion diffusion lengths.

Compared to the $\text{Nb}_2\text{O}_5/\text{rGO}$ nanohybrids, the better performance of the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrid samples may be driven by the following factors. (1) The unique microstructure of the electrode nanoarchitecture. Numerous gullies among the

Fig. 4. Electrochemical performances of nanohybrid-based half-cells. a) CV curves and b) potential profiles of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ electrodes with a potential range of 1.1–3.0 V (Li^+/Li^-); c, d) cycling stability and rate capability of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ and $\text{Nb}_2\text{O}_5/\text{rGO}$ electrodes.

nanoarrays created active sites that were available to the electrolytes. (2) The porousness of the nanoarray microstructure may have shortened the transport path of the ions [55,56]. (3) The amorphous carbon formed by CTAB may have also improved the electric conductivity of (Nb₂O₅@C)/rGO.

3.3. Energy storage mechanism

To obtain more insight into the mechanisms behind the behaviour of the (Nb₂O₅@C)/rGO nanohybrids in different electrolytes, we quantitatively separated the contributions of the capacitive- and faradaic-type elements. Half-cells were prepared in three kinds of electrolytes, commercial organic LiPF₆ electrolyte,

formulated IL electrolyte, and ionogel separator electrolyte, denoted as organic, IL, and ionogel, respectively.

Generally, the relationship between the current rate (i) and the scan rate (v) is expressed by the power law $i = av^b$, where a and b are tunable parameters [57]. Previous studies confirmed that parameter b can be used to denote the kinetics of electrochemical reactions [58]. A b value of 1 suggests that the energy-storage contributions arise primarily from fast near-surface activities, such as charging and discharging in electric double layer capacitor (EDLC). A b value of 0.5 implies a process that is mainly determined by diffusion, as seen in a Li⁺ intercalation battery-type process [16,54]. As illustrated in Fig. 5b, the maximum b values for the anodic and cathodic responses were 0.92 and 0.89, respectively,

Fig. 5. Electrochemical performances of a (Nb₂O₅@C)/rGO electrode in three systems: organic, IL, and ionogel. a) CV curves in the organic system; b) specific current peaks of the three systems within a scanning range of 0.1–1 mV s^{−1}; c–e) CV curves of the capacitive currents (shaded regions) and total current (solid lines) at 1.0 mV s^{−1} in the three systems; f) dependence of the capacitive contribution on various scan rates in different systems; g) Nyquist plots of three different electrolytes at room temperature; h) dependence of capacitive contribution on temperature in the IL system; and i) dependence of the simulated resistances on temperature.

and were achieved in the IL system. The organic system gave b values of around 0.84, close to reported studies [16,59]. The lowest b values, i.e., 0.62 and 0.61 for the anodic and cathodic peak, respectively, were found in the ionogel system. These results imply that the capacitive contribution played the primary role in the energy-storage capability of the IL system, while the contribution of faradaic Li^+ intercalation was the most significant in the ionogel system.

Since the IL and ionogel electrolytes had the same active compounds, i.e., EMIMBF₄ and LiTFSI, the capacitive contribution was quantitatively separated from the diffusion-controlled process using the power law, expressed as [60,61].

$$i(V) = i_{\text{cap}} + i_{\text{diff}} = k_1 v + k_2 v^{1/2} \quad (1)$$

The response current varies linearly with the scan rate (v) when the process is controlled by surface reactions [42,62]. Then, k_1 and k_2 can be evaluated from the slope and intercept of a linear plot of $i/v^{1/2}$ and $v^{1/2}$, respectively, when Eq. (1) is rearranged as [63,64].

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \quad (2)$$

Thus, the current responses contributed by the capacitive effect ($k_1 v$) and by the diffusion-controlled process ($k_2 v^{1/2}$) were quantitatively differentiated [65]. The capacitive contribution of the organic, IL, and ionogel systems were calculated to be 72.5%, 80.1%, and 59.3%, respectively, at 1 mV s^{-1} . In addition, the capacitive contribution ratios of the three systems increased gradually as the scan rate increased (Fig. 5f). Such a trend could be due to the limited Li^+ ions available for a diffusion-controlled reaction in Nb_2O_5 . The IL and ionogel systems had the highest and lowest capacitive contributions, respectively. The highest capacitive contributions that appeared in the IL system were due to the modification of Nb_2O_5 with numerous nanocarbons, which caused significant double-layer charging at relatively high scanning rates. Usually, the sweep rate has relatively little impact on the battery-type process, which is involved in the Li^+ intercalation/deintercalation in the bulk. The ionogel system has a relatively high battery-type process in the $(\text{Nb}_2\text{O}_5/\text{C})/\text{rGO}$ half-cell. Such a phenomenon may be caused by the fact that the migration channels in the ionogel separator were more tortuous, possibly trapping the larger EMIM^+ in the polymer framework and allowing the smaller Li^+ ions to exhibit greater migration. Fig. 5g shows the Nyquist plots of the organic, ionogel, and IL systems, which had simulated electrolyte resistances of 2.6, 4.1, and 20.1Ω , respectively. The enhanced resistance of the IL system was caused by poor wettability between the commercial separator and IL.

The effect of temperature on the storage mechanisms of the IL system was also exploited. All of the capacitive contributions (Fig. 5h) at various scanning rates increased gradually with elevating temperature. Such a pronounced trend may originate from the fastened migration rate of the ions as temperature increased. At enhanced temperatures, more ion pairs in ILs become decoupled; these free ions tend to move faster than coupled pairs in electrolytes [65]. This would allow the large EMIM^+ ions to reach the surfaces of the nanoarchitecture more quickly and generate a capacitive contribution. The Li^+ ions must be intercalated into the crystal lattices in order to generate a faradaic contribution. Electrochemical impedance spectroscopy (EIS) (Fig. S6) was performed at different temperatures to study the effects of temperature. The spectra were simulated by an equivalent circuit (Fig. S7). The resistances of the electrolyte, SEI, and charge transfer are denoted by R_s , R_{p1} , and R_{p2} , respectively [66]. Obviously, all of the impedances declined with increasing temperature. The resistances of the electrolytes and SEI dropped significantly when the temperature was

elevated from 30 to 40°C , accompanied by a significant improvement in the capacitive contribution. Such an anomalous behaviour may be induced by a phase evolution in the formulated IL electrolyte.

A simulation of the molecular dynamics was performed to understand the intrinsic factors that led to an enhanced capacitive contribution in the IL system. The simulation system was constructed inside a cubic box with 300 Li^+ , 300 TFSI^- , 435 EMIM^+ , and 435 BF_4^- ions, which represented the LiTFSI/EMIMBF₄ electrolyte with a mass ratio of 1:1 (Fig. 6a). All MD (molecular dynamics) simulations were realized by using the Gromacs 5.1.1 package, and an OPLS-AA force field was applied for the Li^+ , TFSI^- , EMIM^+ , and BF_4^- ions [45]. The self-diffusion coefficients of the ions at various temperatures were simulated and are plotted in Fig. 6b. As expected, all ions migrated faster with increasing temperature. Generally, the smaller ions moved faster than the bigger ions in the IL system. However, the efficient migration of the larger EMIM^+ ions was even faster than that of the smaller Li^+ ions. Such an anomalous phenomenon was also observed in some other IL systems [67,68]. It was proposed that the smallest Li^+ ions did not diffuse in isolated forms in an IL electrolyte [67]. Previous studies demonstrated that the small Li^+ ions will interact with large anions to form clusters. Fig. 6c and d shows the structures of the Li^+ , BF_4^- , TFSI^- , and EMIM^+ ions, and the possible Li^+ clusters [69,70]. Li^+ was surrounded by a certain number of neighbouring anions. The high solubility of lithium was guaranteed by the energetic penalty induced by the duality between the cations surrounded by a large, unfavourable number of anions, and Li^+ surrounded by a few strongly bound anions. [70] Moreover, the Li^+ transport was not controlled by the exchange of neighbouring Li^+ ions between different anion coordination sites (i.e., an exchange mechanism), but instead was dominated by transport among long-lived Li^+ clusters (i.e., a vehicular mechanism) [69]. As a result, the Li^+ ions exhibited the lowest diffusion coefficient compared the all ions in the IL electrolyte, while the EMIM^+ ions exhibited a relatively large diffusion coefficient. Therefore, nanohybrids modified with two kinds of nanocarbons would display the highest capacitive

Fig. 6. a) Simulated microstructures and b) dependence of the diffusion coefficients of different ions on temperature in the formulated IL electrolyte; c) molecular structure scheme of the Li^+ , EMIM^+ , BF_4^- and TFSI^- ions; and d) a possible configuration of Li^+ clusters in the formulated mixture [69,70].

contribution in the IL electrolyte (Fig. 5f). As expected, the diffusion coefficients of all the ions increased significantly with increasing temperature because they could reach and adsorb on the electrode surface to generate the capacitive process more quickly than at cooler temperatures. This analysis reconfirmed that the capacitive contribution rose with increasing temperature (Fig. 5f).

3.4. Quasi-solid state LICs performance

To further investigate the feasibility of using $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanohybrids for practical applications, quasi-solid-state LICs (SS-LICs) based on an ionogel separator were fabricated. A solution casting was used for the preparation, which withstood an operation potential of up to 4 V. To realize the optimal capacity and rate capability of the SS-LICs, the weight ratio between the active cathode and the anode compound was carefully optimized and fixed at 1.8:1.

A CV test (Fig. 7a) was performed in the cell potential range 0–4 V to analyse the storage processes in the SS-LICs. The deviated rectangular CV curves at a relatively low scanning rate suggest that the fast Li^+ ion intercalation/deintercalation reaction in $\text{T-Nb}_2\text{O}_5$ can match the rapid anion adsorption on the surface of the AC electrode. In addition, the asymmetric CV curves deviated more

from the ideal rectangular shape as the scan rate accelerated due to the discoordination of two energy-storage mechanisms: the fast-non-faradaic adsorption on the AC cathode and the slow faradaic reaction in $\text{T-Nb}_2\text{O}_5$. The GCD profiles (Fig. 7b) reflect a combination of EDLC and LIB, implying an excellent combination of the intercalation reaction and the non-faradaic capacitive storage. The SS-LIC delivered a maximum specific capacitance of 30.6 F g^{-1} with a current density of 0.5 A g^{-1} at 20°C .

LICs are expected to work across a relatively wide temperature range. Furthermore, temperature plays an important role in the viscosity of ILs and the mobility of ions. Therefore, the performances of SS-LICs were evaluated at varied temperatures. The SS-LICs delivered a specific capacitance of 46.8 F g^{-1} at 1 A g^{-1} ; the capacitance remained as high as 23.2 F g^{-1} when the current density was enhanced to 12 A g^{-1} at 60°C (Fig. 7c). Fig. 7d displays the Ragone plots measured at distinct temperatures. The SS-LIC delivered a maximum energy density of 101 Wh kg^{-1} at a power density of 1 kW kg^{-1} , and an energy density of 38.7 Wh kg^{-1} at the maximum power density of 20.7 kW kg^{-1} at 60°C . The improvement in both energy density and power density was ascribed to the enhanced ionic conductivity, which can be expressed by a Vogel-Tamman-Fulcher model [71].

The effect of temperature was also studied via EIS. As plotted in

Fig. 7. Electrochemical performances of $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}/\text{ionogel}/\text{AC}$ quasi-solid-state LIC at various temperatures. a,b) Typical CV curves and GCD profiles collected at 20°C ; c) the specific capacitances versus the current densities at different temperatures; d,e) Ragone plots and Nyquist plots of the quasi-solid-state LIC at different temperatures; and f) the cycling performance collected at 20°C .

Fig. 8. Ragone plots in comparison with reported results. Results from the quasi-solid-state LIC based on $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}/\text{ionogel}/\text{AC}$ at 20 °C and 60 °C were compared with asymmetric supercapacitors $\text{T-Nb}_2\text{O}_5/\text{graphene}/\text{AC}$ [30], $\text{Nb}_2\text{O}_5@\text{C}/\text{AC}$ [43], $\text{Nb}_2\text{O}_5/\text{ionogel}/\text{AC}$ at 60 °C [72], $\text{TiO}_2/\text{ionogel}/\text{AC}$ at 60 °C [73].

Fig. 7e, the semicircles in the high frequency range represent the charge transfer resistance, which decreased from 266.2 to 18.5 Ω as the temperature rose from 20 to 60 °C. In addition, the slopes of the Warburg straight lines in the low frequency range rose gradually with elevating temperature, implying an enhanced Li^+ ion diffusion process. Such a behaviour might originate from the improved ionic conductivity of the electrode at elevated temperatures. The cycling stability study revealed that 83% of the total capacitance was retained after 8000 cycles (Fig. 7f).

Notably, the performances of the current SS-LICs based on an ionogel electrolyte were better than those of previously reported SCs with commercial organic electrolytes. For the sake of comparison, they are compared with selected devices that employed only nanocomposite electrodes or with ionogel electrolyte. Fig. 8 presents the Ragone plots of recently reported asymmetric SCs and those of the devices fabricated for this study. The devices based on an ionogel separator and Nb_2O_5 modified with two kinds of nanocarbons performed better than most previously reported asymmetric SCs [30,43,72,73]. The excellent performance of the current SS-LIC device was likely a result of the following four factors: (1) the ionogel electrolyte effectively widened the operation window up to 4 V; (2) the ionogel separator was capable of withstanding high temperatures with decreased impedance; (3) both the amorphous carbon formed from CTAB and rGO increased the electronic conductivity of the nanohybrids and their interface compatibility with ILs; and (4) the porous microstructure of the $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ electrode not only shortened the diffusion path, but also supplied plenty of active sites on the surface.

4. Conclusion

In summary, complicated $(\text{Nb}_2\text{O}_5@\text{C})/\text{rGO}$ nanoarchitectures were fabricated successfully via a four-step route. Two kinds of modified nanocarbons were found to be critical for the improved interface compatibility and rate performance. The energy-storage mechanisms of the nanoarchitectural electrode were investigated in different electrolytes. A maximum energy density of 101.8 Wh kg^{-1} at 2 kW kg^{-1} and 38.7 Wh kg^{-1} at a large power density of 20.7 kW kg^{-1} were obtained. The remarkable performances of the high-potential ASCs can be attributed to the compatibility of the nanohybrids with the ionogel electrolyte, the synergistic contributions from the ionogel separator, and both the non-faradaic and

faradaic capacitances in the anode. Though many more studies should be conducted to investigate the self-discharging behaviour, this study provides an effective protocol for integrating metal-oxide nanocrystals and several nanocarbons in high-performance energy-storage devices.

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Appendix A. Supplementary data

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