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COMMUNICATION

Lithium-ion batteries based on vertically-aligned carbon nanotube electrodes and ionic liquid electrolytes†

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In conjunction with environmentally benign ionic liquid electrolytes, vertically-aligned carbon nanotubes (VA-CNTs) sheathed with and without a coaxial layer of vanadium oxide (V_2O_5) were used as both cathode and anode, respectively, to develop high-performance and high-safety lithium-ion batteries. The VA-CNT anode and V_2O_5 -VA-CNT cathode showed a high capacity (600 mAh g^{-1} and 368 mAh g^{-1} , respectively) with a high rate capability. This led to potential to achieve a high energy density (297 Wh kg^{-1}) and power density (12 kW kg^{-1}) for the prototype batteries to significantly outperform the current state-of-the-art Li-ion batteries.

Since the first commercialization by Sony Corporation in 1991, lithium-ion (Li-ion) batteries have become the premier rechargeable battery.¹ However, the performance (energy and power densities, safety, and lifetime) of current state-of-the-art Li-ion batteries is still limited by the poor properties of the presently used electrodes and electrolytes. Therefore, there is a need to develop advanced electrode and electrolyte materials to address the performance limitations of Li-ion batteries.

Graphite anodes and lithium cobalt oxide ($LiCoO_2$) cathodes are most frequently used electrode materials for commercial Li-ion batteries. Graphite has a limited capacity (theoretical: 372 mAh g^{-1}) and limited recharge rates.² At rates higher than 1 C, metallic lithium can be plated on the graphite causing a safety hazard. Thus, an optimal anode material for advanced Li-ion batteries should have a higher capacity and higher charge and discharge rates than graphite.³ On the other hand, cobalt-based cathode materials are toxic and expensive.⁴ Only 50% of the theoretical capacity of $LiCoO_2$ could be practically achieved (*i.e.*, 140 mAh g^{-1} vs. 274 mAh g^{-1}). Thus, non-toxic, low-cost, and high-capacity cathode materials are also needed for developing safe and high-energy batteries.

To achieve high energy, high power, and high cyclability for Li-ion batteries, one of the attractive strategies is to develop nanostructured electrode materials with high capacity and high rate capability.^{5–7} In this regard, carbon nanotubes (CNTs) have been studied for battery applications due to their excellent electrical conductivity, large specific surface area, high mesoporosity, and good electrolyte accessibility.^{3,8} Initially, randomly entangled CNTs were used as host materials for direct Li^+ intercalation in anodes^{8,9} or as conductive additives in composite electrodes with graphite.¹⁰ For cathodes, CNTs were studied as conductive additives in composite electrodes with metal oxides¹¹ or as conductive substrates for metal oxide electrodes.^{12,13} In recent years, vertically-aligned architectures have been demonstrated to be a favorable electrode structure for electrochemical energy storage devices, including supercapacitors^{14–18} and batteries.^{7,19–21} Compared to random CNTs, vertically-aligned CNTs (VA-CNTs) with a well-defined regular pore structure and large surface area showed a significantly improved electrolyte accessibility and charge transport capability, making them excellent electrode materials for electrochemical applications. In particular, VA-CNTs have been exploited either directly as electrode materials in supercapacitors^{14–18} and Li-ion batteries (Li^+ intercalation anode)^{7,22} or as conductive substrates for the deposition of electroactive materials (*e.g.*, conducting polymers²³ and metal oxides²⁴) to develop high-capacity and high-rate electrode materials. However, the capacity of functionalized VA-CNTs as electrode materials has barely been exploited.

In addition to the electrode materials, electrolytes are another essential component determining the safety and lifetime of Li-ion batteries. The currently used organic electrolytes have a narrow electrochemical window and are volatile, flammable, and toxic, resulting in poor safety and short lifetime of the existing Li-ion batteries.²⁵ Owing to their unique properties, including a large electrochemical window (up to 6 V), wide liquid phase range (−100 to 400 °C), non-volatility, non-flammability, and non-toxicity, some ionic liquids have recently been studied as a new type of environmentally benign electrolytes to improve the safety and lifetime of Li-ion batteries.^{26–29} Nevertheless, the relatively high viscosity of ionic liquids with respect to conventional aqueous and organic electrolytes is a disadvantage for their electrochemical applications with conventional electrode materials. This drawback can be circumvented by using nanostructured electrodes with

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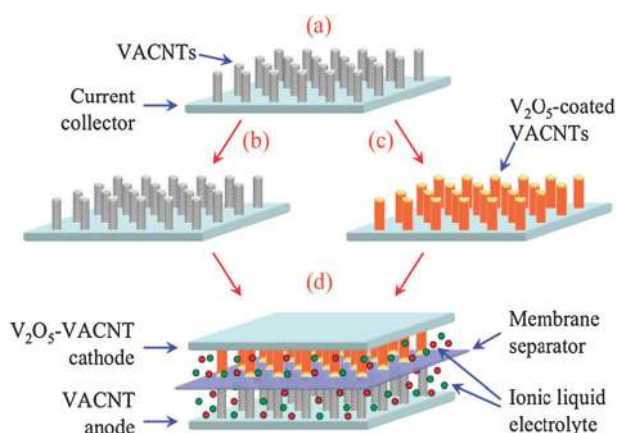


Fig. 1 Schematic representation of a Li-ion battery incorporating vertically-aligned carbon nanotube (VA-CNT) electrodes and ionic liquid electrolyte. (a) Growth of VA-CNTs on a conductive substrate (as current collector). (b) Direct use of VA-CNTs as the anode. (c) Deposition of V₂O₅ on VA-CNTs to synthesize V₂O₅-VA-CNT composite cathode. (d) Assembly of the VA-CNT anode, the V₂O₅-VA-CNT cathode, a membrane separator, and an ionic liquid electrolyte to fabricate the battery. High capacity and high rate capability of the VA-CNT anode and the V₂O₅-VA-CNT cathode ensure a high energy density and a high power density, while superior safety-related properties of ionic liquid electrolytes ensure high safety and long lifetime of the battery thus prepared.

tailor-made porosities to facilitate the diffusion of ionic liquid electrolytes. Our recent research has clearly demonstrated that VA-CNT electrode materials could effectively couple with ionic liquid electrolytes for the development of high-performance supercapacitors.¹⁸

In the present study, we demonstrated that VA-CNTs, in conjugation with environmentally friendly ionic liquid electrolytes, can be used as nanostructured high-capacity and high-rate electrodes for the development of a new class of high-performance and high safety Li-ion batteries. As schematically shown in Fig. 1, we have used VA-CNTs sheathed with and without a coaxial layer of vanadium oxide (V₂O₅) as both cathode and anode, respectively. This is the first time that VA-CNTs were used as both cathode and anode in a Li-ion battery. We found that the VA-CNT anode and the V₂O₅-VA-CNT composite cathode showed a high capacity (600 mAh g⁻¹ and 368 mAh g⁻¹, respectively) with a high rate capability in the ionic liquid electrolyte (*i.e.*, *N*-ethyl-*N,N*-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide, [EDMMEA][TFSI]) used in this study, and that the resultant battery test cells showed a high energy density (297 Wh kg⁻¹) and power density (12 kW kg⁻¹) (estimated from active-material-based performances), possessing the potential to significantly outperform the current state-of-the-art Li-ion battery technology.^{1,27} Furthermore, the use of ionic liquid electrolytes with superior safety-related properties ensures high safety and long lifetime of the newly-developed batteries based on the VA-CNT electrodes and ionic liquid electrolytes. To the best of our knowledge, this is the first time that the multiple drawbacks (*e.g.*, the energy storage, power delivery, safety, and lifetime) associated with the current Li-ion batteries are addressed simultaneously in a single battery system,

opening up a new approach in developing high-performance Li-ion batteries.

In view of the large electrochemical windows of ammonium-based ionic liquids,³⁰ we selected *N*-ethyl-*N,N*-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide ([EDMMEA][TFSI]) to synthesize our electrolytes for Li-ion battery applications. Besides, the wide liquid phase range (−50 to 300 °C), non-volatility, non-flammability, and water-immiscibility of [EDMMEA][TFSI] are additional advantages for developing safe and long-lifetime batteries. After having doped with a Li salt (lithium bis(trifluoromethylsulfonyl)imide, LiTFSI) and a solid electrolyte interface (SEI) film-forming additive (ethylene carbonate, EC), the resultant ionic liquid electrolyte (*i.e.*, 1 M LiTFSI/20% EC/[EDMMEA][TFSI]) showed a high ionic conductivity (3.0 mS cm⁻¹) and a large electrochemical window (5.8 V) (Fig. S1, ESI†).

To minimize the interfacial electrochemical resistance and enhance the interfacial mechanical strength, we directly grew VA-CNTs onto a Ni foil substrate (as the current collector) that was pre-coated with a thin binary layer of Fe (3 nm)/Al (10 nm) as the catalyst for the nanotube growth. The VA-CNT growth was performed by chemical vapor deposition of a gas mixture of 48% Ar, 28% H₂, 24% C₂H₂ at 750 °C for 10–20 minutes (ESI†).³¹ The metal-substrate-supported nanotube growth also ensured the direct use of the resultant VA-CNT/Ni assembly as the electrode, eliminating completely a time-consuming procedure for the electrode preparation with CNTs being transferred from insulating substrates (*e.g.*, SiO₂/Si wafers) typically used for the nanotube growth.³¹ Fig. 2a and b show the well-aligned VA-CNTs with a thin top layer of randomly oriented nanotube segments grown on the Ni foil substrate. Upon plasma etching,³² the top nonaligned carbon layer was removed whilst the structural integrity of the vertically-aligned nanotube trunks was largely retained (Fig. 2c and d). On the other hand, the H₂O-plasma etching also led to a more opened morphology of VA-CNTs (compare (d) with (b) of Fig. 2), possibly due to the water-plasma-induced segregation of the nanotubes,³³ to facilitate the electrochemical deposition of V₂O₅ and the electrolyte access into the nanotube electrode (Fig. 2e and f). The plasma-etched VA-CNT electrode had a tube loading density of ~1.5 mg cm⁻², a tube length of ~600 μm, a tube diameter of 10–15 nm, and a tube spacing of tens to hundreds of nanometers.

In the present work, we used cyclic voltammetry to study the Li⁺ intercalation–deintercalation characteristics and reversibility and used galvanostatic charging–discharging tests to study the rate capability of our electrode materials. Fig. 3a shows well-defined cyclic voltammograms (CVs) for a plasma-etched VA-CNT electrode (as anode) in 1 M LiTFSI/20% EC/[EDMMEA][TFSI]. During the first cathodic scan, an irreversible reduction peak attributable to the reduction of ethylene carbonate^{27–29} appeared at 1.2 V and then disappeared in the following scans due to the formation of a stable SEI film on the VA-CNT electrode. At the first CV cycle, the coulombic efficiency defined by the ratio of oxidation charge to reduction charge of the VA-CNT electrode is low (Fig. 3b). This should be due to the SEI formation as typically observed at a conventional graphite anode.³⁴ The low efficiency observed here is believed to be caused by the high surface area of CNTs

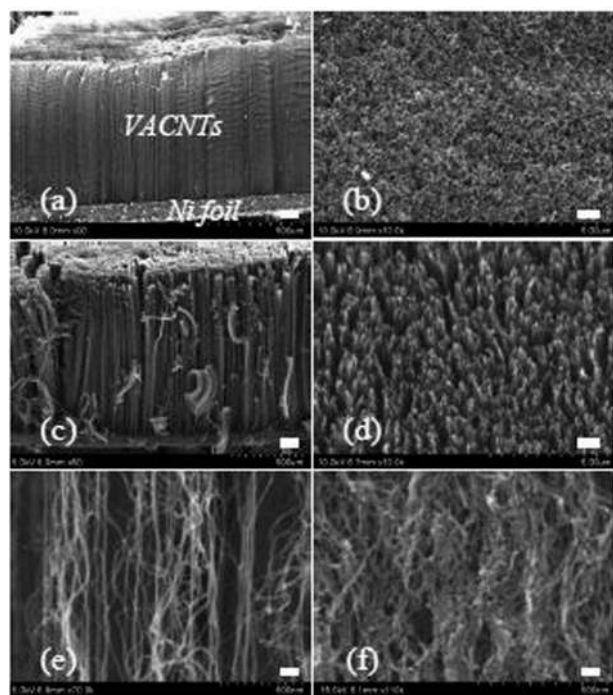


Fig. 2 SEM images of a VA-CNT electrode. (a), (b) Before and (c), (d) after water plasma etching. (a), (c) side view; (b), (d) top view. SEM images of a plasma-etched VA-CNT electrode before (e) and after (f) deposition of V_2O_5 . Note that the micrographs shown in (e) and (f) were not taken from the same spot due to technical difficulties. Scale bar: (a)–(d) 100 μm , (e) and (f) 100 nm. V_2O_5 was deposited on the VA-CNT electrode by potential cycling as described in Fig. S3 (ESI†).

for the SEI formation. Further cycling led to a stable and reversible Li^+ intercalation (at 0 V)–deintercalation (at 0.35 V), and thus an improved columbic efficiency. After 5 cycles, the columbic efficiency reached 98%, indicating a highly reversible Li^+ intercalation–deintercalation process for the VA-CNT electrode, which can be clearly seen in the inset of Fig. 3b. The formation of a stable SEI film and the reversibility of the Li^+ intercalation–deintercalation are essential for a high-performance Li-ion battery anode. Therefore, the plasma-etched VA-CNTs developed in the present study, in conjunction with the ionic liquid electrolyte, are good anode materials for advanced Li-ion batteries. Plasma etching has further removed the top nonaligned carbon layer³⁵ and led to a more porous morphology of the VA-CNT electrode (Fig. 2b and d), which could significantly enhance the Li^+ intercalation–deintercalation process associated with the VA-CNT anode. Indeed, the plasma-etched VA-CNT anode showed much higher and more reversible Li^+ intercalation–deintercalation currents than the pristine VA-CNT anode (Fig. S2, ESI†).

During the galvanostatic charging–discharging at a relatively low rate of 0.25 C, the VA-CNT anode showed a typical Li^+ intercalation plateau at around 0 V, corresponding to a high reversible capacity of 600 mAh g^{-1} (Fig. 3c). Upon the increase in discharge rate, a gradually decreased capacity was observed as expected (e.g., 0.5 C: 471 mAh g^{-1} , 1 C: 422 mAh g^{-1}). Nevertheless, at a rate as high as 2 C, the VA-CNT anode retained the capacity at 365 mAh g^{-1} with a capacity retention up to 61%, indicating a high rate capability.

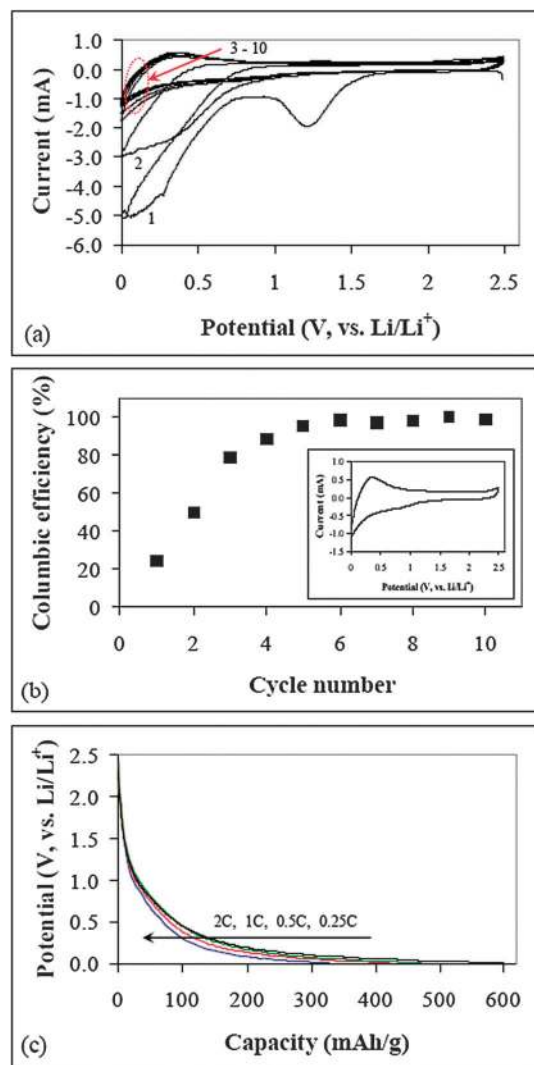


Fig. 3 Cyclic voltammograms (CVs) and corresponding columbic efficiency: (a) CVs and (b) corresponding columbic efficiency of a plasma-etched VA-CNT electrode recorded in 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte. Scan rate: 1 mV s^{-1} . The numbers in (a) represent the number of cycles. The inset in (b) is the 10th cycle of the CV. (c) Discharge curves of the plasma-etched VA-CNT electrode recorded at the rates increasing from 0.25 C to 2 C as indicated by the arrow (curves shown were from the third cycle at each rate). Cut-off potential: 0–2.5 V. Galvanostatic charging–discharging (c) was performed for the same VA-CNT electrode after its CV test (a).

It should be noted that considerable research has been reported in the literature about the development of high-rate Li^+ intercalation anodes (mostly with conventional electrolytes). Taking into account the relatively higher viscosity and lower conductivity of ionic liquids compared to conventional electrolytes, the rate performance of our VA-CNT anode in the present work should be considered to be reasonably high, which should be attributed to the unique porous structures of the VA-CNTs. As illustrated in Fig. 1, each of the constituent aligned tubes of a VA-CNT electrode is directly connected onto a common current collector. The vertically-aligned nanotubes with a well-defined large surface area, high mesoporosity, and intimate contact to the current collector should allow for a

rapid charge–discharge process collectively through each of the individual nanotubes within the VA-CNT electrode. Therefore, the high-rate capability of the VA-CNTs for Li^+ intercalation–deintercalation could ensure a high power of Li-ion batteries, as reflected by the high-power supercapacitors previously reported with the VA-CNTs.¹⁸ Furthermore, a separate continuous charging–discharging test (up to 100 cycles) did not show significant capacity degradation for the VA-CNT electrode, indicating its good stability as anode in the ionic liquid electrolyte selected.

Anodes based on randomly-oriented CNTs have been previously shown to suffer from undesirable voltage hysteresis between charging and discharging associated with the slow kinetics and poor reversibility of the Li^+ intercalation–deintercalation process. Attempts have been made to eliminate this problem, for example, by cutting the nanotubes into short segments to improve the charge transport capability of the electrode.³⁶ Compared with a randomly-oriented CNT electrode in a conventional organic electrolyte with a potential separation of ~ 0.9 V between the Li^+ intercalation and deintercalation,³⁷ our results clearly show a much smaller potential separation (0.35 V, inset of Fig. 3b), and hence a low voltage hysteresis for the VA-CNT electrodes even in an ionic liquid electrolyte with a relatively high viscosity. Along with the high coulombic efficiency, therefore, the well-defined alignment and tube spacing, enhanced electrolyte accessibility, and rapid charge transport capability intrinsically associated with the VA-CNTs have made the Li^+ intercalation–deintercalation highly reversible at the VA-CNT anode, ensuring an improved cycle life for batteries.

In order to synthesize a high-capacity and high-rate cathode to match the high-performance VA-CNT anode necessary for developing batteries of high-energy and high-power, we deposited V_2O_5 as a coaxial thin film around each of the individual plasma-etched VA-CNTs to produce the V_2O_5 –VA-CNT composite cathode (Fig. 1c). Owing to its high safety, low cost, and high theoretical capacity (590 mAh g^{-1} , corresponding to four moles of Li^+ intercalated into per mole of V_2O_5), V_2O_5 has been investigated as a potential high-performance cathode material to replace LiCoO_2 for Li-ion batteries.^{38,39} However, the low electronic conductivity (10^{-6} – $10^{-7} \text{ S cm}^{-1}$)⁴⁰ of and the slow Li^+ diffusion (diffusion coefficient: $\sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$)⁴¹ through V_2O_5 have severely limited its electrochemical storage application. Although V_2O_5 thin films have been used as preferred cathode materials for miniaturized batteries in microsystems to address the above drawbacks and some efforts have been made to deposit V_2O_5 thin films onto (random) CNT paper substrates for large size applications,^{12,13} decreased capacity and rate performance were observed for the resultant V_2O_5 –CNT electrodes, due possibly to the limited surface area and irregular porous structure of the random CNTs. The use of electrically conducting VA-CNTs with a large surface area for coaxial coating with V_2O_5 ensures a relatively large V_2O_5 loading even in a thin film form resulting in the large capacity and high rate capability of the V_2O_5 –VA-CNT composite cathode (Fig. 2f). The nanotube's good conductivity also facilitates the electrochemical deposition of V_2O_5 coaxially around each of the constituent CNTs in the plasma-etched VA-CNTs (ESI†). The V_2O_5 loading for the V_2O_5 –VA-CNT composite electrode

was optimized by varying the number of potential cycles during the electrodeposition of V_2O_5 (Fig. S4, ESI†). A low V_2O_5 mass loading (0.14 mg cm^{-2}) produced a very high capacity of 690 mAh g^{-1} (defined by V_2O_5 mass) for the composite electrode. This value of capacity is even higher than the theoretical one for pure V_2O_5 (590 mAh g^{-1})⁴² and has been attributed to the combined energy storage arising from both the redox process of V_2O_5 and the double-layer charging of the CNT substrate.^{12,13,18} Increasing V_2O_5 loading up to 2.25 mg cm^{-2} resulted in an enhanced capacity even defined by the overall mass of the V_2O_5 –VA-CNT composite (Fig. S4, ESI†). However, further increase in the V_2O_5 loading blocked the spaces between the tubes of the VA-CNTs, leading to a reduced capacity for the V_2O_5 –VA-CNT composite electrode. The best deposition condition was optimized to be 80 potential cycles for the V_2O_5 electrodeposition to yield a capacity of 368 mAh g^{-1} for the resultant V_2O_5 –VA-CNT composite electrode. The V_2O_5 loading was about 60% in the V_2O_5 –VA-CNT composite, a value that is higher than that on a random CNT paper substrate.^{12,13} The well-defined high surface area associated with VA-CNTs is believed to be responsible for the observed high (and efficient) V_2O_5 %loading for the V_2O_5 –VA-CNT composite electrode. Without blocking the intertube space (Fig. 2f), the high V_2O_5 %loading means a high capacity and a high rate capability of the V_2O_5 –VA-CNT composite electrode.

Fig. 4a shows three pairs of reversible redox peaks, attributable to the known three-step successive phase transformations during the Li^+ insertion and extraction of V_2O_5 ,⁴³ for the V_2O_5 –VA-CNT composite cathode in 1 M LiTFSI/20% EC/[EDMMEA][TFSI]. Moreover, the envelope shape of the obtained CV should be due to the capacitive behavior of the high surface area and high porosity of V_2O_5 , as reported previously.⁴⁴ Importantly, this indicates the proper Faradic and capacitive properties of the electrochemically synthesized V_2O_5 coaxial layer on the VA-CNT substrate in the present work. Unlike the VA-CNT anode, the V_2O_5 –VA-CNT composite electrode rapidly reached its highest coulombic efficiency of 99% after the first initial cycle without the formation of a SEI film (Fig. 4b). During galvanostatic charging–discharging at 0.25 C, the V_2O_5 –VA-CNT composite electrode showed a high capacity of 368 mAh g^{-1} (Fig. 4c). At a higher rate, a capacitor-like discharge behavior (linear potential decline without a plateau) was observed. At 2 C, the V_2O_5 –VA-CNT composite electrode retained the capacity at 230 mAh g^{-1} (capacity retention: 63%), showing its high rate capability. Again, with respect to the relatively high viscosity and low conductivity of ionic liquids (compared to conventional electrolytes), this rate performance should be considered to be reasonably high and can be attributed to the unique porous structures of the VA-CNTs. Further charging–discharging (100 cycles) did not cause significant fading in capacity for this composite electrode, suggesting its good stability as cathode in the ionic liquid electrolyte studied.

It should be noted that V_2O_5 , as an alternative cathode material to LiCoO_2 , has been largely studied in conventional organic electrolytes. Only very little research on the electrochromic behavior of V_2O_5 thin films in ionic liquid electrolytes has been reported.⁴⁵ The present work demonstrated for the

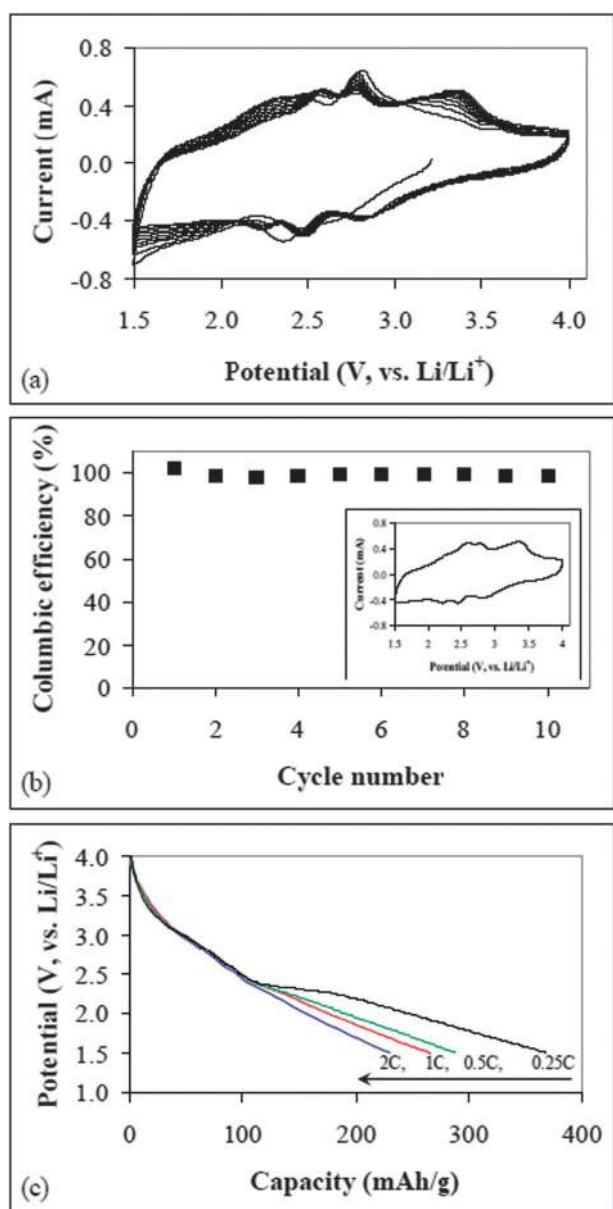


Fig. 4 Cyclic voltammograms (CVs) and corresponding columbic efficiency: (a) CVs and (b) corresponding columbic efficiency of a V_2O_5 -VA-CNT electrode recorded in 1 M LiTFSI/20% EC/[EDMMEA][TFSI] electrolyte. Scan rate: 1 mV s^{-1} . The inset in (b) is the 10th cycle of the CV. (c) Discharge curves of the V_2O_5 -VA-CNT electrode recorded at the rates increasing from 0.25 C to 2 C as indicated by the arrow (curves shown were from the third cycle at each rate). Cut-off potential: 1.5–4 V. Galvanostatic charging–discharging (c) was performed for the same V_2O_5 -VA-CNT electrode after its CV test (a). The V_2O_5 -VA-CNT electrode was prepared by potential cycling as described in Fig. S3 (ESI †).

first time the good match between the V_2O_5 -VA-CNT composite electrode and the ionic liquid electrolyte for developing high-performance Li-ion batteries.

To study the performance of full battery cells, we fabricated the VA-CNT anode, the V_2O_5 -VA-CNT composite cathode, and the ionic liquid electrolyte (1 M LiTFSI/20% EC/[EDMMEA][TFSI]) into prototype batteries (ESI †). Due to the fact that the as-synthesized VA-CNT anode and

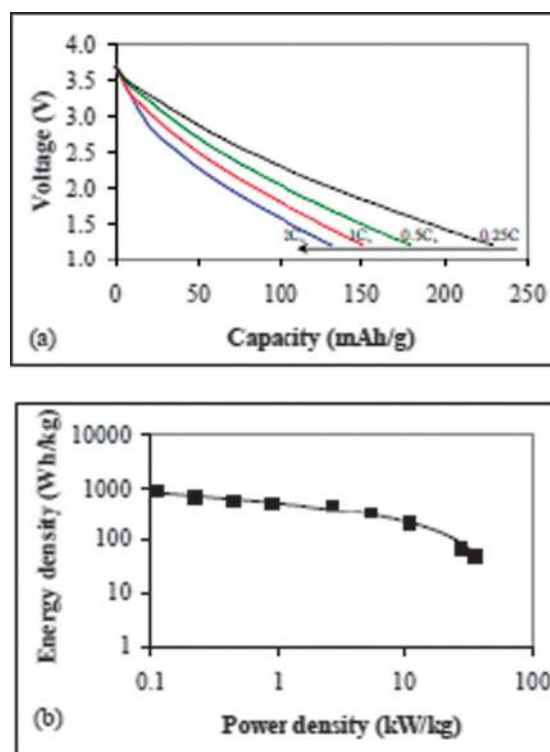


Fig. 5 (a) Discharge curves of a VA-CNT/ V_2O_5 -VA-CNT battery recorded at the rates increasing from 0.25 C to 2 C as indicated by the arrow. The capacity is defined by the total active-material-mass of the anode and the cathode. Cut-off voltage: 1.2–3.7 V. (b) Ragone plot of the VA-CNT/ V_2O_5 -VA-CNT battery. Performance of the battery is defined by the total active-material-mass of the VA-CNT anode and the V_2O_5 -VA-CNT cathode.

V_2O_5 -VA-CNT cathode do not contain lithium, a pretreatment is necessary to pre-lithiate one of these electrode materials prior to the assembly of a battery full cell. This can be done by electrochemically pre-lithiating either the VA-CNT anode or the V_2O_5 -VA-CNT cathode. For our preliminary proof-of-concept study in the present work, we pre-lithiated the VA-CNT anode by electrochemical potential cycling (ESI †). In addition to lithiation, this pretreatment can also ensure a high columbic efficiency of the VA-CNT anode prior to its use for full cell assembly. It was found that these batteries could store a large amount of energy and rapidly deliver the stored energy to achieve a high power (Fig. 5). Unlike a traditional Li-ion battery where the discharge is characterized by a voltage plateau followed by a sharp voltage drop at the end of discharge, the VA-CNT based batteries developed in this study showed a supercapacitor-like linear voltage decline at a fixed rate (Fig. 5a), indicating their capability to be discharged all the way down to the fully discharged state. For most conventional batteries, the achievement of a high power sacrifices their energy storage capacity. This has been a long-time problem that makes the Li-ion battery technology unfavorable for high-rate applications (*e.g.*, electric vehicles). Along with recent intensive research efforts in developing Li-ion batteries with both high energy and high power,^{5,6} we have developed the VA-CNT-based batteries to show the potential to achieve the great promise, with a maximum energy density of 847 Wh kg^{-1} and a maximum power density

of 35 kW kg⁻¹ (Fig. 5b). Based on a simplified estimation method,⁴⁶ these active-material-based data can be converted to the corresponding values (energy density: 297 Wh kg⁻¹, power density: 12 kW kg⁻¹) for a packaged battery, possessing the potential to significantly exceed those of the current Li-ion batteries.¹ Volumetric performance of these prototype batteries (energy density: 95 Wh L⁻¹, power density: 4 kW L⁻¹) is not as promising as their gravimetric performance, which is believed to be determined by the low packing density of VA-CNTs, a common phenomenon for nanomaterials. Furthermore, in order to make these new batteries practically useful in terms of volumetric performance, our future work will investigate approaches (e.g., high-density-packing⁴⁷) to enhance nanotube loading for VA-CNT electrodes. Upon the improvement in volumetric performance of electrodes, we will design and fabricate prototype batteries with carefully balanced loading between the anode and cathode in order to achieve a long cycle life. Moreover, the excellent safety-related properties of ionic liquid electrolytes and the environmental stability of V₂O₅ and CNTs will ensure an inherently safe operation and long lifetime of these batteries.

In summary, we have for the first time used VA-CNTs sheathed with and without a coaxial layer of vanadium oxide (V₂O₅) as both cathode and anode, respectively, in a Li-ion battery. We found that the VA-CNT anode and the V₂O₅-VA-CNT composite cathode showed a high capacity (600 mAh g⁻¹ and 368 mAh g⁻¹, respectively) with a high rate capability in an ionic liquid electrolyte (i.e., *N*-ethyl-*N,N*-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl)imide, [EDMMEA][TFSI]). By integrating these electrode and electrolyte materials, we have demonstrated prototype batteries with a high energy density (297 Wh kg⁻¹) and power density (12 kW kg⁻¹) (estimated from active-material-based performances) to be attractive for high-rate applications (e.g., electric vehicles). The use of environmentally benign ionic liquid electrolytes can further ensure high safety and prolonged lifetime of the batteries. The present work offers a promising approach to high-performance Li-ion batteries with significantly improved energy, power, and safety.

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Notes and references

- R. J. Brodd, K. R. Bullock, R. A. Leising, R. L. Middaugh, J. R. Miller and E. Takeuchi, *J. Electrochem. Soc.*, 2004, **151**, K1.
- Advances in Lithium-ion Batteries*, ed. W. A. van Schalkwijk and B. Scrosati, Kluwer Academic/Plenum Publishers, 2002, pp. 79–101.
- E. Frackowiak and F. Beguin, *Carbon*, 2002, **40**, 1775.
- Z. Chen, W. Q. Lu, J. Liu and K. Amine, *Electrochim. Acta*, 2006, **51**, 3322.
- K. Kang, Y. S. Meng, J. Breger, C. P. Grey and G. Ceder, *Science*, 2006, **311**, 977.
- P. Poizot, S. Laurelle, S. Grugeon, L. Dupont and J.-M. Tarascon, *Nature*, 2000, **407**, 496.
- M. Durstock, D. Welna, B. Taylor, L. Dai and L. Qu, *J. Power Sources*, 2010, **196**, 1455, and references cited therein.
- G. Che, B. B. Lakshmi, E. R. Fisher and C. R. Martin, *Nature*, 1998, **393**, 346.
- Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, American Scientific Publishers, 2003, vol. X, pp. 1–19.
- M. Endo, T. Hayashi and Y.-A. Kim, *Pure Appl. Chem.*, 2006, **78**, 1703.
- L. Wang, Y. Huang, R. Jiang and D. Jiaz, *J. Electrochem. Soc.*, 2007, **154**, A1015.
- I.-H. Kim, J.-H. Kim, B.-W. Cho and K.-B. Kim, *J. Electrochem. Soc.*, 2006, **153**, A989.
- I.-H. Kim, J.-H. Kim, B.-W. Cho and K.-B. Kim, *J. Electrochem. Soc.*, 2006, **153**, A1451.
- Q. L. Chen, K. H. Xue, W. Shen, F. F. Tao, S. Y. Yin and W. Xu, *Electrochim. Acta*, 2004, **49**, 4157.
- C. Du, J. Yeh and N. Pan, *Nanotechnology*, 2005, **16**, 350.
- Y. Honda, T. Haramoto, M. Takeshige, H. Shiozaki, T. Kitamura and M. Ishikawa, *Electrochem. Solid-State Lett.*, 2007, **10**, A106.
- H. Zhang, G. Cao, Y. Yang and Z. Gu, *J. Electrochem. Soc.*, 2008, **155**, K19.
- W. Lu, L. Qu, K. Henry and L. Dai, *J. Power Sources*, 2009, **189**, 1270.
- P. L. Taberna, S. Mitra, P. Poizot, P. Simon and J.-M. Tarascon, *Nat. Mater.*, 2006, **5**, 567.
- P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845.
- A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda and P. M. Ajayan, *Nano Lett.*, 2009, **9**, 1002.
- G. X. Wang, J. Yao, H. K. Liu, S. X. Dou and J.-H. Ahn, *Met. Mater. Int.*, 2006, **12**, 413.
- M. Hughes, M. S. P. Shaffer, A. C. Renouf, C. Singh, G. Z. Chen, D. J. Fray and A. H. Windle, *Adv. Mater.*, 2002, **14**, 382.
- H. Zhang, G. Gao, Z. Wang, Y. Yang, Z. Shi and Z. Gu, *Nano Lett.*, 2008, **8**, 2664.
- K. Xu, *Chem. Rev.*, 2004, **104**, 4303.
- A. Lewandowski and A. Swiderska-Mocek, *J. Power Sources*, 2009, **194**, 601.
- M. Holzapfel, C. Jost and P. Novak, *Chem. Commun.*, 2004, 2098.
- B. Garcia, S. Lavalley, G. Perron, C. Michot and M. Armand, *Electrochim. Acta*, 2004, **49**, 4583.
- H. H. Zheng, H. C. Zhang, Y. B. Fu, T. Abe and Z. Ogumi, *J. Phys. Chem. B*, 2005, **109**, 13676.
- V. Borgel, E. Markevich, D. Aurbach, G. Semrau and M. Schmidt, *J. Power Sources*, 2009, **189**, 331.
- H. Chen, A. Roy, J.-B. Baek, L. Zhu, J. Qu and L. Dai, *Mater. Sci. Eng., R*, 2010, **70**, 63, and references cited therein.
- S. Huang and L. Dai, *J. Phys. Chem. B*, 2002, **106**, 3543.
- See, for example: S. H. Li, H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, L. Jiang and D. B. Zhu, *J. Phys. Chem. B*, 2002, **106**, 9274.
- Advances in Lithium-ion Batteries*, ed. W. A. van Schalkwijk and B. Scrosati, Kluwer Academic/Plenum Publishers, 2002, pp. 7–77.
- L. Qu, L. Dai, M. Stone, Z. Xia and Z. L. Wang, *Science*, 2008, **322**, 238.
- P. M. Ajayan and O. Z. Zhou, Applications of Carbon Nanotubes, *Top. Appl. Phys.*, 2001, **80**, 391; *Carbon Nanotubes*, ed. M. S. Dresselhaus, G. Dresselhaus and Ph. Avouris, Springer-Verlag, Berlin Heidelberg, 2001.
- J. Chen, A. I. Minett, Y. Liu, C. Lynam, P. Sherrell, C. Wang and G. G. Wallace, *Adv. Mater.*, 2008, **20**, 566.
- D. B. Lee, S. Passerini, A. L. Tipton, B. B. Owens and W. H. Smyrl, *J. Electrochem. Soc.*, 1995, **142**, L102.
- K. Salloux, R. Chaput, H. R. Wong, B. Dunn and M. W. Breiter, *J. Electrochem. Soc.*, 1995, **142**, L191.
- M. Benmoussa, E. Ibnuouelghazi, A. Bennouna and E. L. Ameziane, *Thin Solid Films*, 1995, **265**, 22.
- S. Passerini, J. J. Ressler, D. B. Le, B. B. Owens and W. H. Smyrl, *Electrochim. Acta*, 1999, **44**, 2209.
- D. B. Le, S. Passerini, J. Guo, J. Ressler, B. B. Owens and W. H. Smyrl, *J. Electrochem. Soc.*, 1996, **143**, 2099.
- C. Delmas, S. Brethes and M. Menetrier, *J. Power Sources*, 1991, **34**, 113.
- W. Dong, D. R. Rolison and B. Dunn, *Electrochem. Solid-State Lett.*, 2000, **3**, 457.
- A. Brazier, G. B. Appetechi, S. Passerini, A. S. Vuk, B. Orel, F. Donsanti and F. Decker, *Electrochim. Acta*, 2007, **52**, 4792.
- M. Mastragostino, C. Arbizzani, R. Paraventi and A. Zanelli, *J. Electrochem. Soc.*, 2000, **147**, 407.
- N. Futaba, K. Hat, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura and S. Iijima, *Nat. Mater.*, 2006, **5**, 987.