ARTICLE

Surface functionalized 3D carbon fibers boosts the lithium storage behaviour of transition metal oxide nanowires via strong electronic interaction and tunable adsorption energy

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Lei Hu,^{b†} Yingxia Gao,^{a†} Tuzhi Xiong,^a David Adekoya,^c Weitao Qiu,^b Hao Yang,^b M.-Sadeeq (Jie Tang) Balogun,^{*a} Shanqing Zhang,^c Anlian Pan,^a Yuping Li,^{*a} and Yexiang Tong^{*b}

The Li-ion storage properties of transition metal oxide (TMOs) electrodes such as Li-ion intercalation-based electrodes are usually enhanced by hybridizing with 3D carbon scaffolds. However, understanding on the large variation of performance enhancement is rarely reported. As a proof of concept, intercalation reaction-based TMOs (V₂O₅ and TiO₂) nanowires were hybridized with two types of 3D carbon scaffolds (namely pristine carbon fiber cloth, CFC and porous N-doped CFC, PNCFC). Theoretical calculation predicts that the PNCFC@TMOs hybrids displayed reasonable lower adsorption energy towards easier Li-ion intercalation than those of CFC@TMOs. Electrochemical properties further disclosed that PNCFC-based hybrids exhibit the best lithium storage performance. Furthermore, *in situ* Raman, XPS and charge redistribution studies not only decipher that strong electronic interaction exists between PNCFC and TMOs but also consistently affirm that such interaction is ascribed to the shift of the p-adsorption energy, facilitating rapid kinetics and leading to improved Li storage properties.

Introduction

Li-ion intercalation reaction (LiIR)-based electrodes are one of the most promising electrode materials for lithium ion batteries (LIBs) because they offer the advantages of low volume expansion, stable solid electrolyte interface layer formation, little irreversible capacity loss and no electrolyte decomposition.^{1–5} The intercalation reaction of TMOs is shown as follows:⁶

Transition metal oxides (TMOs)^{7–9} such as Ti oxides-based^{10, 11} electrodes especially TiO₂ and V oxides-based^{12–15} electrodes especially V₂O₅ usually exhibit such LiIR mechanism. Meanwhile, these TMOs exhibit either poor electrochemical stability (V₂O₅) or poor electrical conductivity (V₂O₅ and TiO₂) leading to loss in capacity and low rate capability, respectively.^{16, 17} In order to improve the dual dilemma of both V₂O₅ and TiO₂, one of the common strategies employed is to design self-supporting electrode materials by the direct growth of the active materials on 3D carbon scaffolds (e.g. carbon cloth, graphene, carbon nanotubes and so on).^{18–22} Such strategy could automatically prevent the intercalation of Li-ion into carbon scaffold (Li-ion usually intercalates in carbon-based material at a working potential below 1.0 V) and make it easy to determine the capacity contribution of the active V₂O₅ and TiO₂ materials. Previous literature has shown that the performance enhancement of the carbon scaffolds and TMOs hybrids can be attributed to the conductive 3D network and high surface area that allows rapid ion/electron transfer, enhanced conductivity and improved mechanical flexibility.^{19, 23} However, despite the enhanced storage properties,²⁴ the understanding on the intrinsic properties of the carbon scaffold and active electrodes is rarely reported.^{25, 26} In addition, less or no attention is given to the theoretical insight on the effect of such hybridization towards enhanced electrochemical activity.²⁷

In this work, density functional theory (DFT) calculations were first studied to probe the intercalation of Li-ion into V₂O₅ on pristine carbon fiber cloth (CFC) and porous N-doped carbon fiber cloth (PNCFC). The PNCFC-based sample requires lower adsorption energy to complete intercalation process than the CFC counterparts. CFC was selected among the commonly reported carbon scaffolds owing to its good mechanical strength, stability, and wide application in energy storage researches.^{24, 27–29} Electrochemical performance of PNCFC@V₂O₅ presents superior Li storage properties over CFC@V₂O₅. *In situ* Raman spectra and XPS consistently reveal that there exist strong electronic interaction between PNCFC and V₂O₅, which is valuable towards improving Li storage

^a College of Materials Science and Engineering, Hunan University, Changsha 410082, P.R. China. E-mail: balogun@hnu.edu.cn; liypli@hnu.edu.cn

^b MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-carbon Chemistry & Energy Conservation of Guangdong Province, KLGHEI of Environment and Energy Chemistry, School of Materials Science and Engineering, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, P.R. China. E-mail: chedhx@mail.sysu.edu.cn

^c Centre for Clean Environment and Energy, Griffith School of Environment, Gold Coast Campus, Griffith University, QLD 4222, Australia.

[†] These authors contribute equally.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

kinetics. Such strong electronic interaction allows the downshift of p-band adsorption center that is favorable for enhancing the Li storage performance. More interestingly, based on the understanding of PNCFC@V₂O₅, theoretical and experimental analyses further verifies that hybrid of TiO₂ and PNCFC can also display similar phenomenon by modulating the p-orbital adsorption energy.

Results

Theoretical Predictions

Previous literature has reported that series of TMOs directly synthesized on 3D carbon scaffolds usually relate the enhanced performance to the 3D network.^{19, 29, 30} However, theoretical studies on the intercalation process of carbon compared to the active materials in their powdery forms are rarely studied. DFT calculations were first employed to investigate the optimum Gibbs free energy change (ΔG_{H^+}) required for Li-ion diffusion through pristine V₂O₅ and CFC@V₂O₅.^{31, 32} The diffusion barrier during diffusion process of Li-ion is very essential for understanding the electrode behaviour and the reasons for enhanced Li-ion storage performance.^{33, 34} The optimized cluster structures of V₂O₅ and CFC@V₂O₅ for the DFT calculations can be found in (Supporting information, Figure S1 and S2) and the free energy change diagrams of V₂O₅ and CFC@V₂O₅ are shown in Figure 1a and 1b, respectively. The free energy change diagrams for these three electrodes are derived based on theoretical intercalation of Li-ions (i.e. lithiated state) into these electrodes. For example, Figure S3 shows the lithiated state of V₂O₅, while Figures S4 and S7 also show the lithiated state of both CFC@V₂O₅ and PNCFC@V₂O₅, respectively. Li-ion at the initial state (Figures S3-I and S4-I) accounts for ΔG_{H^+} of 0.0 eV in both electrodes (Figure 1a-i and 1b-iii). At the V₂O₅ surface, CFC@V₂O₅ requires a lower diffusion barrier of 0.14 eV (Figure S4-II and 1b-ts-3), whereas the ΔG_{H^+} is much higher in V₂O₅ (0.19 eV, Figure S3-II and 1a-ts-1). Upon complete Li-ion intercalation into the lattice of the electrodes forming Li_xV₂O₅ (Figure S3-III), V₂O₅ will still have to overcome an energy barrier of 1.81 eV (Figure 1a-ts-2). The lower diffusion barrier

(ΔG_{H^+}) of 0.95 eV (Figures 1b-ts-4 and S4-III) for CFC@V₂O₅ compared to that of pristine V₂O₅ indicates that rapid Li-ion transportation and enhanced kinetics throughout the intercalation process and could result in superior performance of CFC@V₂O₅ over pristine V₂O₅. Finally, the energy barrier of V₂O₅ and CFC@V₂O₅ returned to 0.0 eV (Figure 1a-ii and 1b-iv) after the entire intercalation process (Figure S3-IV and S4-IV), respectively.

Previously, we have shown that the surface of CFC can be functionalized with nitrogen (N) atoms, high porosity, and better conductivity, which leads to high surface area and also serves as promising anode materials for LIBs.^{27, 35} When the porous N-doped functionalized CFC (denoted as PNCFC) was used as a current collector for the growth of conversion reaction-based TMOs such as NiCo₂O₄, experimental and theoretical analyses confirmed that there exists an electronic interaction between PNCFC and NiCo₂O₄, which is responsible for achieving high capacity of the hybrid.²⁷ Additionally, V₂O₅ nanobelts³⁶ and V₂O₅ nanosheets³⁷ cathodes that were synthesized on graphene foam and carbon nanotubes (CNTs) displayed enhanced performance due to the 3D network and harmonious integration.^{36, 37} Motivated by this concept, we utilized the PNCFC as a current collector for the direct synthesis of V₂O₅ nanowires (denoted as PNCFC@V₂O₅ NWs) and compare its performance with that of CFC@V₂O₅ NWs.

Theoretical predictions on PNCFC@V₂O₅ hybrid was conducted based on the optimized structure model for PNCFC@V₂O₅ (Figure S5). The enlarged snapshot of covalent bonds between C (a functional group of PNCFC) and O (from V₂O₅), and between O (functional group of PNCFC) and V (from V₂O₅) are depicted in Figure S6a and S6b, respectively. This bonding shows that the functional groups revealed a close relationship between individual elements in the electrode. Compared to CFC@V₂O₅, the optimum Gibbs free energy change (ΔG_{H^+}) required for Li-ion transportation in PNCFC@V₂O₅ is shown in Figure 1c. During Li-ion intercalation in PNCFC@V₂O₅ (Figure S7), the ΔG_{H^+} at ts-5 and ts-6 are 0.06 and 0.35 eV, also indicating the complete lithiated state of V₂O₅, and significantly lower than those of CFC@V₂O₅ and pristine V₂O₅.

Figure 1. Calculated migration ΔG_{H^+} to Li-ion diffusion through (a) V₂O₅, (b) CFC@V₂O₅ and (c) PNCFC@V₂O₅ from DFT calculations.

The result further suggests that the support of functionalized 3D carbon scaffold with TMOs could not only hastens Li-ion diffusion pathway and enhances the kinetics but also lowers the adsorption energy towards achieving high performance LIBs.

Synthesis and Morphological Characterization

The scanning electron microscopy (SEM) images of the two current collectors, CFC and PNCFC (highly networked self-supported current collectors) are shown in Figure S8a and S8b, respectively. The direct growth of V_2O_5 NWs on the CFC and PNCFC self-supported materials was accomplished through hydrothermal and air-annealing treatments as previously reported.¹⁹ Schematic illustrations of V_2O_5 NWs fabrication process can be seen in Scheme S1 (details about synthetic method can be found in the experimental section). Firstly, a 24 cm² piece of CFC was converted to PNCFC through hydrothermal reaction, thermal reduction and etching treatments (Scheme S1-I).³⁸ SEM image clearly shows the porous and rough nature of the PNCFC surface as seen in Figure 2a. Transmission electron microscopy (TEM) analysis further reveals an exfoliated and porous surface on the PNCFC (Figure 2a inset). For the CFC current collector, the approximate thickness of a single fiber is 9.6 μ m (Figure S9a), which reduces to 7.7 μ m after modification to PNCFC (Figure S9b).

Previous reports have demonstrated that lightweight substrates or current collectors with porous morphology could serve as favorable scaffolds for the growth of active materials, while reducing the weight of the entire cell^{24, 36, 39} and also contributed to the flexible properties of the electrodes.^{24, 35, 40, 41} Thus, VO_x NWs (Figure S10) were synthesized on both CFC and PNCFC current collectors and annealed at 400 °C in the air to obtain CFC@ V_2O_5 (Scheme S1-II) and PNCFC@ V_2O_5 NWs (Scheme S1-III), respectively.

According to the XRD pattern, both samples were characterized with V_2O_5 peaks (JCPDF Card #65-0131) but there's no significant differences in the phases of the two samples (Figure S11). Both the SEM images for CFC@ V_2O_5 and PNCFC@ V_2O_5 consist of interwoven NWs with diameters in the range of 300-800 nm (Figures S12 and 2b), respectively. Figure 2c clearly depicts that V_2O_5 NWs were successfully coated on the smooth surface of CFC, while Figure 2d affirms the growth of the NWs firmly adhered to the PNCFC current collector. Further information regarding the morphology of the adhesiveness of V_2O_5 NWs and PNCFC current collector interface was accomplished by TEM analyses. Interestingly, the TEM images revealed three-layer (core-double shell) architecture of the sample (Figures 2e and S13), consisting of inner-core CFC layer, exfoliated carbon middle-shell layer and V_2O_5 NWs outer-shell layer. Energy dispersive X-ray spectroscopy (EDS) elemental mapping collected from Figure 2e with its corresponding HAADF (Figure 2f) displayed the distribution of C (Figure 2g-red), V (Figure 2h-yellow) and O (Figure 2i-blue) and N (Figure 2j-orange). Figure 2g discloses that the intensity of C (red colour) decreases from bulk (top side) to the surface (down side) and the presence of V and O at the outermost shell layer (Figure 2h) also confirms the formation of V_2O_5 . The results obtained from the EDS analyses further certified that the V_2O_5 NWs were successfully coated on a PNCFC current collector demonstrating a core-double shell design. Additionally, TEM image collected from PNCFC@ V_2O_5 NWs surface (Figure 2k) showed the single crystalline nature (Figure S14) and lattice spacing of 0.34 nm (Figure 2l), which corresponds to the (110) plane of V_2O_5 and also affirms the successful formation of V_2O_5 on PNCFC substrate.

Electronic Structure Characterization

The electronic structure and valence states of both CFC@ V_2O_5 and PNCFC@ V_2O_5 and more information on the relationship between V_2O_5 and the two types of current collectors were studied using X-ray photoelectron spectroscopy (XPS). The XPS survey spectra of CFC@ V_2O_5 and PNCFC@ V_2O_5 can be found in Figure S15a. C 1s of the PNCFC@ V_2O_5 exhibited a broad signal for the C-C bond and additional broad peak compared to the CFC@ V_2O_5 sample, which suggests some extent of modifications in the modified CFC coated samples (Figure 3a).^{35, 42} Moreover, a peak at ~400 eV in the N 1s spectra of PNCFC@ V_2O_5 is totally absent in CFC@ V_2O_5 sample (Figure 3b). This confirmed that that PNCFC@ V_2O_5 sample is N-doped. The N-doping can be obtained during thermal reduction of $Ni(OH)_2 \cdot 0.75H_2O$ precursor in N_2 atmosphere.^{27, 38} Compared to the V 2p XPS spectra of CFC@ V_2O_5 , the V 2p XPS spectra of both samples can be deconvoluted into two synthetic peaks (516.3 eV for V^{4+} and 517.6 eV for V^{5+}) (Figure 3c-I and 3c-II) confirming that the V_2O_5 samples are mixed-valence in nature.⁴³⁻⁴⁷ Interestingly, the V^{5+} V 2p XPS spectra of CFC@ V_2O_5 , shifted to a lower binding energy (ca. 0.36 eV) in PNCFC-based sample, whereas, the V^{4+} V 2p XPS spectra shifted to a lower binding energy (ca. 0.36 eV) for the PNCFC-based sample.

Figure 2. Morphological characterization. (a) SEM image of PNCFC showing the exfoliated porous surface. Inset is the corresponding TEM image. (b) SEM image of PNCFC@ V_2O_5 showing V_2O_5 NWs. (c) SEM image of CFC@ V_2O_5 showing the contact between CFC and V_2O_5 . (d) SEM image of PNCFC@ V_2O_5 showing V_2O_5 NWs strictly adhered to the PNCFC surface. (e) TEM image of PNCFC@ V_2O_5 NWs showing the core-double shell-like architecture. Elemental mapping of PNCFC@ V_2O_5 showing distribution of the elements from (f) HAADF, (g) C, (h) V, (i) O, and (j) N. (k) TEM image of PNCFC@ V_2O_5 NWs and (l) HRTEM image of PNCFC@ V_2O_5 NWs displaying the lattice fringes.

Figure 3. (a) C 1s, (b) N 1s and (c) V 2p_{3/2} XPS spectra of CFC@V₂O₅ and PNCFC@V₂O₅.

This phenomenon indicates change in the electronic bonding environment state, justifies strong electronic

interaction between PNCFC and V₂O₅ and suggests rapid transfer of electrons in PNCFC@V₂O₅ sample.^{27, 48} Moreover, the higher shift in the binding energy of the V⁴⁺ suggests stronger electronic interaction on the low valence state of PNCFC@V₂O₅, which could be beneficial for enhancing the sample conductivity and kinetics.⁴⁹ Additionally, the percentage ratio of the V⁴⁺/V⁵⁺ in the samples increased from 38% in CFC@V₂O₅ to 47% in PNCFC@V₂O₅ sample, meaning that a higher composition of V⁴⁺ improved the electronic interactions between V₂O₅ and PNCFC, which could also be an avenue for improving the electrochemical performance of PNCFC@V₂O₅.⁴³

It has been previously proposed that the valence of vanadium oxides composites can be tailored, and could be a promising way to achieve high capacity, good conductivity and good cycling stability.^{44, 45} For instance, self-doped of V⁴⁺ into V₂O₅ nanoflakes exhibit high structural stability, long-term and fast reversible Li storage capability resulting from the presence of V⁴⁺.⁴³ Likewise V₂O₅ xerogels showed improved lithium storage performance benefiting from the multi-vanadium oxidation states and electrical conductivity.⁵⁰ Thus, we proposed that the high composition of V⁴⁺ in PNCFC@V₂O₅ arises from the electronic interaction between V₂O₅ and PNCFC, and this could eventually lead to improving the electrochemical performance of PNCFC@V₂O₅ over CFC@V₂O₅ sample. According to Figure S15b, the O 1s XPS spectra of PNCFC@V₂O₅ is slightly different from that of CFC@V₂O₅, also confirming that characteristic functional groups from PNCFC current collector and such functional groups are beneficial in improving electrode kinetic properties.^{27, 51} Based on the *Ex situ* Raman spectroscopy analyses, the entire Raman peak below 1000 cm⁻¹ corresponds with V₂O₅ Raman peaks reported in other literature (Figure S16a).⁵² More importantly, the Raman spectra presents a D:G peak intensity ratio of 1.48 for PNCFC@V₂O₅ and also larger than that of the CFC@V₂O₅ (1.32) (Figure S16b). In addition, the G-band of PNCFC@V₂O₅ sample becomes broader further affirming modification of the treated CFC coated sample. This can be attributed to the porous exfoliated surface of the PNCFC substrate that consists of some surface disorder and presence of functional groups induced by etching, which is in agreement with the O 1s XPS spectra.^{35, 53}

Li-Storage Properties

Li storage behaviour and performance for both CFC@V₂O₅ and PNCFC@V₂O₅ positive electrodes was studied in a coin cell. The Li-ion insertion-deinsertion reactions in V₂O₅ can be seen from the 5th cyclic voltammetry (CV) curves for both electrodes (Figure S17) and the corresponding reaction mechanism can be seen as V₂O₅ + xLi⁺ + xe⁻ ⇌ Li_xV₂O₅.³⁶ Regular peaks of V₂O₅ can be found in both electrodes.⁵⁴ PNCFC@V₂O₅ electrode shows stronger current density peaks than the CFC@V₂O₅ electrode and also shift to higher voltage region, which implies that PNCFC@V₂O₅ electrode has a higher electrochemical reactivity and enhanced conductivity than the CFC@V₂O₅.³⁶ Electrochemical impedance spectroscopy (EIS) analysis was carried out to have insight information on the kinetics of both CFC@V₂O₅ and PNCFC@V₂O₅ electrodes.

Figure 4. Li storage properties. (a) The Nyquist plots, (b) charge-discharge curves at a current density of 2.0 C, (c) rate capability and (d) cyclic stability at a current density of 2.0 C of both CFC@V₂O₅ and PNCFC@V₂O₅. (e) *In-situ* Raman spectra of PNCFC@V₂O₅ at different intercalated voltages. (f) The plot of the I_D/I_G vs. intercalated voltages of CFC@V₂O₅ and PNCFC@V₂O₅.

The Nyquist plot is characterized with a semi-circle and diffusion slope representing the charge transfer resistance (R_{ct}) and Warburg impedance, respectively.¹⁹ The smaller the R_{ct} , the more the increase in the electron transfer rate of V₂O₅ in PNCFC@V₂O₅ cell. As seen in Figure 4a, PNCFC@V₂O₅ displays smaller R_{ct} value (86 Ω) than that of CFC@V₂O₅ (122 Ω), confirming the superior conductivity of PNCFC@V₂O₅ electrode over CFC@V₂O₅. As shown in Figure 4b, the discharge capacity of PNCFC@V₂O₅ is 268 mAh g⁻¹ after 10th electrochemical cycle, while that of CFC@V₂O₅ is lower (233 mAh g⁻¹). It should be noted that energy efficiency (%) is a vital parameter for the practical development of new electrode materials. The energy efficiency of a battery usually depends on the overpotentials of charging and discharging profiles and can be determined according to the formula below;⁵⁵

$$\text{Energy efficiency} = \frac{\text{Energy density}_{(\text{discharge})}}{\text{Energy density}_{(\text{charge})}} \times 100\% \quad (2)$$

The energy density is determined by the area under the charge-discharge curves. According to Figure 4b, the energy efficiency of CFC@V₂O₅ and PNCFC@V₂O₅ are approximately 95%, which can still be maximized for practical interest.⁵⁵ Figure 4c demonstrated the rate capability performance of PNCFC@V₂O₅ and CFC@V₂O₅ electrodes. With increasing current density from 0.3C to 17C, PNCFC@V₂O₅ electrode

continuously displayed superior performance over CFC@V₂O₅ electrode. Unlike CFC@V₂O₅ electrode with capacity retention of 69% at 17C, PNCFC@V₂O₅ electrode performance delivered a reversible capacity of 233 mAh g⁻¹ (81% capacity retention) at current rate of 17C. A clear difference can be observed with PNCFC@V₂O₅ electrode retaining a specific capacity of 243 mAh g⁻¹ (85% capacity retention) with 100% coulombic efficiency, while its counterpart could only deliver 192 mAh g⁻¹ (75% capacity retention) at the same testing current density of 17C for 500 cycles (Figure 4d). It can be observed that both electrodes show fast capacity decay in the first 20 cycles. Generally, the main problem of bulk V₂O₅ as electrode material for LIBs is its poor cyclic stability and rate capability. Thus, the fast capacity decay in the first 20 cycles for both the electrodes is a common phenomenon to V₂O₅. The SEM images of PNCFC@V₂O₅ electrode after stability test confirmed that the V₂O₅ NWs were still strongly adhered to the surface of the PNCFC current collector (Figure S18). These results further verify the exemplary stability of the PNCFC@V₂O₅ electrode.

In-situ Raman Analysis

Additional analysis on the intercalation of Li-ion was done by *in-situ* Raman spectra for the two electrodes. Raman analysis is an effect strategy to study the effect of defect carbon and graphitic carbon in a sample.²⁷ Detail process on the set-up can be found in Figure S19. The response of the current collectors D and G peaks towards Li-ion intercalation at different voltages can be effective for determining the impact of the different CFC current collectors. The Raman spectra collected for CFC@V₂O₅ showed a non-uniform variation in its carbon D and G bands at different Li-ion voltages (Figure S19e), while that of PNCFC@V₂O₅ showed nearly uniform variations in the D and G bands (Figure 4e). The I_D/I_G values of the electrodes are plotted against the intercalation at different voltages (Figure 4f) and the I_D/I_G value of PNCFC@V₂O₅ cell is nearly the same at different Li-ion voltages, but varies and non-uniform for CFC@V₂O₅. This result interprets that the V₂O₅ NWs are not strictly attached to the CFC surface leading to instability of CFC@V₂O₅ electrode. However, the I_D/I_G values for PNCFC@V₂O₅ indicate that there are strong interfacial interactions between the shell layer of the PNCFC and V₂O₅ NWs. These interactions are highly stable regardless of the voltage. Such strict adherence between the PNCFC and V₂O₅ NWs allows easy diffusion of Li-ion and transportation of electrons into the entire electrode cavity. Both the theoretical analyses and experimental results are consistent and also account for the higher capacity retention and better stability of the PNCFC@V₂O₅ electrode over the CFC@V₂O₅.

Discussion

Charge Redistribution and Adsorption Energy Capability

The electronic interaction between V₂O₅ and PNCFC demonstrates a crucial role in enhancing the Li-storage properties of PNCFC@V₂O₅. DFT calculations were further employed to investigate the charge distribution relationship between V₂O₅ and carbon scaffolds. The optimized model

structures for $\text{CFC@V}_2\text{O}_5$ and $\text{PNCFC@V}_2\text{O}_5$ are displayed in Figures S2 and S5, respectively. Figure 5a distinctly displayed the natural bonding orbital (NBO) charge distribution in the optimized $\text{CFC@V}_2\text{O}_5$ and $\text{PNCFC@V}_2\text{O}_5$ obtained from DFT calculations.

Figure 5. (a) NBO charge redistribution of V_2O_5 , $\text{CFC@V}_2\text{O}_5$ and $\text{PNCFC@V}_2\text{O}_5$. (b) DOS plots of CFC and PNCFC and their corresponding p-bands. (c) DOS plots of $\text{CFC@V}_2\text{O}_5$ and $\text{PNCFC@V}_2\text{O}_5$ and their corresponding p-bands.

The NBO charge distribution of pristine V_2O_5 was also introduced for comparison (optimized model structure in Figure S1). The charge distribution on $\text{PNCFC@V}_2\text{O}_5$ shows that the positive charge on V is less electropositive, while the negative charge on O is less electronegative, in the order of $\text{PNCFC@V}_2\text{O}_5 > \text{CFC@V}_2\text{O}_5 > \text{V}_2\text{O}_5$. However, the positive charge on C of $\text{PNCFC@V}_2\text{O}_5$ is more electropositive. These results indicate that the surface functionalization of PNCFC could change the electron density charges on the entire electrode, leading to excellent electronic interactions between PNCFC and V_2O_5 compared to that of $\text{CFC@V}_2\text{O}_5$.²⁷ To obtain further understanding on the electronic interaction between the hybrids, the analysis of the density of states (DOS) related to the Fermi level (E_f) is studied and the corresponding s, p, d, f and sum bands DOS are shown in Figure S20. Firstly, in all the samples, the p-band is more intense than those s, d and f-bands and nearly the same with that of the sum-adsorption energy, indicating that the main Li-ion intercalation process is related to the p-adsorption energy. The p-adsorption energy center (E_p) relative to E_f of CFC is -1.27 eV and that of PNCFC is -6.43 eV (Figure 5b). The results indicate that E_p of PNCFC is farther away from the E_f , facilitating the energy band-gap to reduce and allowing p-band to undergo distinct shift in PNCFC than CFC. The hybridization of PNCFC with V_2O_5 could definitely require lower adsorption energy than that of CFC-based hybrids. Indeed, the E_p in $\text{PNCFC@V}_2\text{O}_5$ also depicts a shift towards high E_f (-10.52 eV) than $\text{CFC@V}_2\text{O}_5$ (-10.21 eV) (Figure 5c) due to the increased bonding strength of PNCFC-based hybrid, that originates from the easy release and pulling of electrons from of $\text{PNCFC@V}_2\text{O}_5$. Hence, the energies of the charge density and valence band electrons will increase, enabling rapid electron transfer towards promoting fast Li-ion intercalation kinetics for enhanced Li-ion storage properties. Finally, both the NBO charge distribution and DOS results indicate changes in the bonding or electronic states and also in accordance with the XPS, finally affirming that there exist a stronger electronic interactions between PNCFC and V_2O_5 than pristine CFC and V_2O_5 .

TiO₂-Based Anode: Electrochemical Properties and Mechanism Studies

To obtain further understanding of the LiIR-based mechanism, we also utilized TiO_2 anode, which is also well known for its poor electrical conductivity leading to its slow kinetics and poor rate capability. Similar to V_2O_5 , theoretical predictions on TiO_2 hybridized with CFC and PNCFC were studied. DFT calculations conducted to determine the ΔG_{H^+} required for Li-ion intercalation through CFC@TiO_2 and PNCFC@TiO_2 . The optimized CFC@TiO_2 and PNCFC@TiO_2 cluster structures used for DFT calculations are presented in Figures S21 and S22, respectively. As Li-ion passes across the optimized CFC@TiO_2 structure (Figure S23), the ΔG_{H^+} required for the transportation of Li-ion throughout CFC@TiO_2 is 1.11 eV (Figure 6a). However, the maximum ΔG_{H^+} required is 0.51 eV for PNCFC@TiO_2 to transport the Li-ion through the entire PNCFC@TiO_2 structure

Figure 6. Properties of CFC@TiO₂ and PNCFC@TiO₂. (a) Calculated migration ΔG_{H^+} to Li-ion diffusion through CFC@TiO₂ and PNCFC@TiO₂. (b) NBO charge redistribution of CFC@TiO₂ and PNCFC@TiO₂. (c) SEM images of PNCFC@TiO₂ NWs. (d) Rate performance and (e) Plot of the I_d/I_g vs. intercalated voltages for CFC@TiO₂ and PNCFC@TiO₂. (f) DOS plots of TiO₂, CFC@TiO₂ and PNCFC@TiO₂ and their corresponding p-bands.

(Figure S24), which is also lower than that of CFC@TiO₂. These results also correlate with that of V₂O₅ in Figure 1. NBO charge distribution studies were also performed for the TiO₂-based electrodes. Pristine TiO₂ was also employed for comparison (optimized structure in Figure S25). The enlarged snapshot of covalent bonds between O (a functional group of ECC) and Ti (from TiO₂) and an enlarged snapshot of covalent bonds between C (a functional group of ECC) and O (from TiO₂) are shown in Figure S26.

According to the NBO charge redistribution in Figure 6b, compared to CFC@TiO₂ and pristine TiO₂, the charge value on the positively charged Ti decreases, the positive charge on C increases and negatively charged O in PNCFC@TiO₂, indicating that stronger electronic interactions between PNCFC and TiO₂ of PNCFC@TiO₂. Hence, we hydrothermally coated Rutile-type TiO₂ nanowires (TiO₂ NWs) (Figure S27) on CFC (CFC@TiO₂ NWs) and PNCFC (PNCFC@TiO₂ NWs) according to our previous work (Figure 6c).^{11, 16} Because TiO₂ is known for its poor electrical conductivity, the rate capability performance was performed at different current densities and in the voltage range of 1.0–3.0 V (vs. Li/Li⁺), where the PNCFC@TiO₂ exhibited superior storage properties to CFC@TiO₂ (Figure 6d). *In-situ* Raman spectra also shows that the PNCFC@TiO₂ is more stable than CFC@TiO₂ (Figure 6e). Furthermore, the plot of I_d/I_g values against intercalation voltages collected from the whole results obtained for TiO₂-based are in-line with those of V₂O₅-based electrodes. Moreover, the E_p of PNCFC@TiO₂ is -5.67 eV, which is also farther from the E_f compared to CFC@TiO₂ (Figure 6f), indicating a shift in the E_p , and could facilitate rapid

Li-ion kinetics in PNCFC@TiO₂ than CFC@TiO₂. Hence, these results did not clearly confirm the Li-ion storage properties of LiIR-based TMO electrodes can be effectively modulated by tuning the p-adsorption energy level but also deciphered understanding on the large variation of performance enhancement in carbon scaffold-TMO electrode hybrids.

Conclusions

In summary, we systematically demonstrated the theoretical and experimental insights on the storage mechanism and large variation in the Li-ion storage performance of different carbon scaffolds as current collectors for LiIR-based TMO electrodes. LiIR-based electrodes, such as V₂O₅ and TiO₂ NWs, were directly synthesized on two different carbon current collectors with different surface properties (CFC and PNCFC). DFT calculations revealed that Li-ion adsorption occurred at lower adsorption energy (ΔG_{H^+}) level of 7.75 and 4.64 eV for PNCFC@V₂O₅ and PNCFC@TiO₂, respectively compared to those of CFC@V₂O₅ (18.21 eV), V₂O₅ (29.04 eV), CFC@TiO₂ (6.67 eV) and TiO₂ (11.34 eV). Electrochemical performance confirmed that the V₂O₅ and TiO₂ NWs coated on PNCFC exhibited better Li-storage activity than those hybridized on CFC. Additionally, in-situ Raman spectra analysis revealed PNCFC could serve as a better scaffold for the electrodes in enhancing the cyclic stability and rate capability of the PNCFC-based electrodes than CFC. XPS, NBO charge distribution and DOS analyses showed that the PNCFC-based electrodes are attributed to stronger electronic interaction between the

PNCFC and TMOs due to the shift of p-adsorption energy level. This work deciphers insight into the Li-storage mechanism and performance modulation of carbon-based current collectors and LiIR-based electrodes.

Conflicts of interest

"There are no conflicts to declare".

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21875292 and 51525202), National Key Research and Development Program of China (2016YFA0202604), the Fundamental Research Funds for the Central Universities (17lgjc36) and Science Starting Foundation of Hunan University (531118010182).

References

1. T. Zhou, Y. Zheng, H. Gao, S. Min, S. Li, H. K. Liu and Z. Guo, *Adv. Sci.*, 2015, **2**, 1500027.
2. V. Aravindan, Y.-S. Lee and S. Madhavi, *Adv. Energy Mater.*, 2015, **5**, 1402225.
3. S. Cao, Z. Xue, C. Yang, J. Qin, L. Zhang, P. Yu, S. Wang, Y. Zhao, X. Zhang and R. Liu, *Nano Energy*, 2018, **50**, 25-34.
4. S. Joshi, Q. Wang, A. Puntambekar and V. Chakrapani, *ACS Energy Lett.*, 2017, **2**, 1257-1262.
5. Z. Yao, X. Xia, D. Xie, Y. Wang, C.-a. Zhou, S. Liu, S. Deng, X. Wang and J. Tu, *Adv. Funct. Mater.*, 2018, **28**, 1802756.
6. X. Xia, D. Chao, C. F. Ng, J. Lin, Z. Fan, H. Zhang, Z. X. Shen and H. J. Fan, *Mater. Horiz.*, 2015, **2**, 237-244.
7. X. Xia, S. Deng, S. Feng, J. Wu and J. Tu, *J. Mater. Chem. A*, 2017, **5**, 21134-21139.
8. F. Wang, X. Wang, Z. Chang, Y. Zhu, L. Fu, X. Liu and Y. Wu, *Nanoscale Horiz.*, 2016, **1**, 272-289.
9. C. Wang, L. Wu, H. Wang, W. Zuo, Y. Li and J. Liu, *Adv. Funct. Mater.*, 2015, **25**, 3524-3533.
10. V. Augustyn, E. R. White, J. Ko, G. Grüner, B. C. Regan and B. Dunn, *Mater. Horiz.*, 2014, **1**, 219-223.
11. M.-S. Balogun, M. Yu, C. Li, T. Zhai, Y. Liu, X. Lu and Y. Tong, *J. Mater. Chem. A*, 2014, **2**, 10825-10829.
12. Y. Dai, Q. Li, S. Tan, Q. Wei, Y. Pan, X. Tian, K. Zhao, X. Xu, Q. An, L. Mai and Q. Zhang, *Nano Energy*, 2017, **40**, 73-81.
13. Y. Yue and H. Liang, *Adv. Energy Mater.*, 2017, **7**, 1602545.
14. J. Yao, Y. Li, R. C. Massé, E. Uchaker and G. Cao, *Energy Stor. Mater.*, 2018, **11**, 205-259.
15. S. Wang, K. A. Owusu, L. Mai, Y. Ke, Y. Zhou, P. Hu, S. Magdassi and Y. Long, *Appl. Energy*, 2018, **211**, 200-217.
16. M.-S. Balogun, C. Li, Y. Zeng, M. Yu, Q. Wu, M. Wu, X. Lu and Y. Tong, *J. Power Sources*, 2014, **272**, 946-953.
17. B. Long, M.-S. Balogun, L. Luo, Y. Luo, W. Qiu, S. Song, L. Zhang and Y. Tong, *Small*, 2017, **13**, 1702081.
18. L. Shen, B. Ding, P. Nie, G. Cao and X. Zhang, *Adv. Energy Mater.*, 2013, **3**, 1484-1489.
19. M.-S. Balogun, Y. Luo, F. Lyu, F. Wang, H. Yang, H. Li, C. Liang, M. Huang, Y. Huang and Y. Tong, *ACS Appl. Mater. Interfaces*, 2016, **8**, 9733-9744.
20. Y. Shi, L. Wen, G. Zhou, J. Chen, S. Pei, K. Huang, H. M. Cheng and F. Li, *2d Mater.*, 2015, **2**, 024004.
21. S. Yoon, S. Lee, S. Kim, K.-W. Park, D. Cho and Y. Jeong, *J. Power Sources*, 2015, **279**, 495-501.
22. G. Qian, X. Liao, Y. Zhu, F. Pan, X. Chen and Y. Yang, *ACS Energy Lett.*, 2019, **4**, 690-701.
23. X. Min, B. Sun, S. Chen, M. Fang, X. Wu, Y. g. Liu, A. Abdelkader, Z. Huang, T. Liu, K. Xi and R. Vasant Kumar, *Energy Stor. Mater.*, 2019, **16**, 597-606.
24. S. Liu, Z. Wang, C. Yu, H. B. Wu, G. Wang, Q. Dong, J. Qiu and A. Eychmüller, *Adv. Mater.*, 2013, **25**, 3462-3467.
25. Y. Deng, S. Dong, Z. Li, H. Jiang, X. Zhang and X. Ji, *Small Methods*, 2018, **2**, 1700332.
26. X. Huang, G. Diao, S. Li, M.-S. Balogun, N. Li, Y. Huang, Z.-Q. Liu and Y. Tong, *RSC Adv.*, 2018, **8**, 17056-17059.
27. M.-S. Balogun, H. Yang, Y. Luo, W. Qiu, Y. Huang, Z.-Q. Liu and Y. Tong, *Energy Environ. Sci.*, 2018, **11**, 1859-1869.
28. H.-p. Feng, L. Tang, G.-m. Zeng, J. Tang, Y.-c. Deng, M. Yan, Y.-n. Liu, Y.-y. Zhou, X.-y. Ren and S. Chen, *J. Mater. Chem. A*, 2018, **6**, 7310-7337.
29. M.-S. Balogun, M. Yu, Y. Huang, C. Li, P. Fang, Y. Liu, X. Lu and Y. Tong, *Nano Energy*, 2015, **11**, 348-355.
30. G. X. Pan, X. H. Xia, F. Cao, J. Chen and Y. J. Zhang, *Electrochim. Acta*, 2014, **149**, 349-354.
31. Y. Chu, L. Guo, B. Xi, Z. Feng, F. Wu, Y. Lin, J. Liu, D. Sun, J. Feng, Y. Qian and S. Xiong, *Adv. Mater.*, 2018, **30**, 1704244.
32. Y. Zheng, T. Zhou, X. Zhao, W. K. Pang, H. Gao, S. Li, Z. Zhou, H. Liu and Z. Guo, *Adv. Mater.*, 2017, **29**, 1700396.
33. J. Hu, C. Ouyang, S. A. Yang and H. Y. Yang, *Nanoscale Horiz.*, 2019, **4**, 457-463.
34. S. Ullah, P. A. Denis and F. Sato, *Appl. Mater. Today*, 2017, **9**, 333-340.
35. M.-S. Balogun, W. Qiu, F. Lyu, Y. Luo, H. Meng, J. Li, W. Mai, L. Mai and Y. Tong, *Nano Energy*, 2016, **26**, 446-455.
36. D. Chao, X. Xia, J. Liu, Z. Fan, C. F. Ng, J. Lin, H. Zhang, Z. X. Shen and H. J. Fan, *Adv. Mater.*, 2014, **26**, 5794-5800.
37. D. Kong, X. Li, Y. Zhang, X. Hai, B. Wang, X. Qiu, Q. Song, Q.-H. Yang and L. Zhi, *Energy Environ. Sci.*, 2016, **9**, 906-911.
38. M.-S. Balogun, W. Qiu, H. Yang, W. Fan, Y. Huang, P. Fang, G. Li, H. Ji and Y. Tong, *Energy Environ. Sci.*, 2016, **9**, 3411-3416.
39. X. Fang, M. Ge, J. Rong and C. Zhou, *ACS Nano*, 2014, **8**, 4876-4882.
40. K. Wang, S. Luo, Y. Wu, X. He, F. Zhao, J. Wang, K. Jiang and S. Fan, *Adv. Funct. Mater.*, 2013, **23**, 846-853.
41. D. Chao, C. Zhu, X. Xia, J. Liu, X. Zhang, J. Wang, P. Liang, J. Lin, H. Zhang and Z. X. Shen, *Nano Lett.*, 2014, **15**, 565-573.
42. W. Wang, W. Liu, Y. Zeng, Y. Han, M. Yu, X. Lu and Y. Tong, *Adv. Mater.*, 2015, **27**, 3572-3578.
43. H. Song, C. Liu, C. Zhang and G. Cao, *Nano Energy*, 2016, **22**, 1-10.
44. S. D. Perera, B. Patel, N. Nijem, K. Roodenko, O. Seitz, J. P. Ferraris, Y. J. Chabal and K. J. Balkus, *Adv. Energy Mater.*, 2011, **1**, 936-945.
45. Y. Song, T.-Y. Liu, B. Yao, T.-Y. Kou, D.-Y. Feng, X.-X. Liu and Y. Li, *Small*, 2017, **13**, 1700067.
46. Y. Huang, Y. Lu, Y. Lin, Y. Mao, G. Ouyang, H. Liu, S. Zhang and Y. Tong, *J. Mater. Chem. A*, 2018, **6**, 24740-24747.
47. Y. Huang, L. Hu, R. Liu, Y. Hu, T. Xiong, W. Qiu, M. S. Balogun, A. Pan and Y. Tong, *Appl. Catal. B-environ*, 2019, **251**, 181-194.
48. Y. Sun, K. Xu, Z. Wei, H. Li, T. Zhang, X. Li, W. Cai, J. Ma, H. J. Fan and Y. Li, *Adv. Mater.*, 2018, **30**, 1802121.

49. G. Diao, M.-S. Balogun, S.-Y. Tong, X. Guo, X. Huang, Y. Mao and Y. Tong, *J. Mater. Chem. A*, 2018, **6**, 15274-15283.
50. D. Liu, Y. Liu, A. Pan, K. P. Nagle, G. T. Seidler, Y.-H. Jeong and G. Cao, *J. Phys. Chem. C*, 2011, **115**, 4959-4965.
51. K. Ye, K. Li, Y. Lu, Z. Guo, N. Ni, H. Liu, Y. Huang, H. Ji and P. Wang, *TrAC Trends in Anal. Chem.*, 2019, **116**, 102-108.
52. M. Gotić, S. Popović, M. Ivanda and S. Musić, *Mater. Lett.*, 2003, **57**, 3186-3192.
53. G. Wang, H. Wang, X. Lu, Y. Ling, M. Yu, T. Zhai, Y. Tong and Y. Li, *Adv. Mater.*, 2014, **26**, 2676-2682.
54. P. Zhang, L. Zhao, Q. An, Q. Wei, L. Zhou, X. Wei, J. Sheng and L. Mai, *Small*, 2016, **12**, 1082-1090.
55. A. Eftekhari, *Sustainable Energy Fuels*, 2017, **1**, 2053-2060.