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Titanium carbide-decorated graphite felt as high performance negative electrode in vanadium redox flow batteries

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This paper presents a novel method for preparing binder-free, uniformly distributed titanium carbide (TiC) nanoparticles on graphite felt (GF) surfaces for use as negative electrode in an all vanadium redox flow battery (VRFB). TiO₂ particles were grown on the surface of the GF using hydrothermal synthesis and were subsequently converted to TiC by way of a carbothermal reaction. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and VRFB single cell tests unequivocally confirm the catalytic effect of TiC towards the negative redox couple V²⁺/V³⁺. A VRFB employing a TiC-decorated electrode in the negative half-cell exhibited a 13% gain in energy efficiency (EE) at a current density of 100 mA cm⁻², compared to reference cells assembled solely with pristine graphite felts. Moreover, VRFB cells employing the modified electrode show excellent stability with high capacity retention over repetitive cycling. These results suggest that TiC nanoparticles supported on carbon fibres constitute a high performance negative electrode for VRFBs.

1 Introduction

The vanadium redox flow battery (VRFB) is regarded as one of the promising technologies for large-scale energy storage. The primary benefits of the VRFB are associated with its flexibility with respect to the rating of power and storage time, low-maintenance cost and prolonged life time.¹ The unique feature of the VRFB is the separation of the power-generating stack and energy-carrying electrolyte, which permits the decoupling of energy capacity and power output. In a VRFB, V²⁺/V³⁺ and VO²⁺/VO₂⁺ dissolved in H₂SO₄ serve as the negative and positive redox couples respectively. Since both negative and positive electrolytes contain only vanadium species, the imbalance from the cross-contamination of the electrolyte poses no risk, as the desired redox species can be electrochemically regenerated.²⁻⁴ Carbon-based materials, mostly polyacrylonitrile (PAN)-based GFs, are widely used as electrode materials in VRFB due to their favourable characteristics, such as three-dimensional structure, resistance to corrosion, high porosity, high electronic conductivity and low cost.⁵ Previous studies have reported that despite the high surface area, GFs commonly require further modification for better wettability and enhancement of the reaction kinetics.⁶ As a result, various modification methods to

activate GF for use as an electrode in VRFB have been explored. Among these methods, thermal treatment is the most widely used technique.⁷ There have also been attempts to oxidise the GF by way of wet chemical methods using oxidisers, such as sulfuric acid, nitric acid or a mixture of both.⁸ Other approaches, such as plasma etching, exposure to ozone or ammonia have also been proposed to create more active sites.^{9,10} These treatments promote the formation of oxygen and nitrogen-containing functional groups, which produce favourable effects on the reaction kinetics. In particular, surface oxygen complexes have been shown to play a crucial role for the negative electrode.¹¹

An alternative method for improving the charge transfer kinetics is to deposit a catalyst onto the surface of the electrode. This approach was reported some time ago during the early development of iron-chromium flow batteries by NASA in the 1970s.¹² While using catalyst-functionalised electrodes in a VRFB, several aspects should be taken into consideration, such as the susceptibility of hydrogen evolution in the negative half-cell, stability of the catalyst in the highly acidic environment and the uniform distribution of the catalyst throughout the electrode volume. Furthermore, the method used for the deposition of the catalyst plays an essential role, since the catalysts need to bind effectively to the surface of the carbon fibre in order to warrant electronic contact. The catalyst should show sufficient stability against dissolution or electrochemically-induced aging. Finally, the cost and availability of the catalyst constitute prerequisites for practical application.

Noble metals, such as Pt, Ir, Mn, Pd, and Au deposited on carbon fibres were studied during the early development of the VRFB by the Skaylas-Kazacos group.¹³ As expected, hydrogen

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evolution was prominent for Pt, Au and Pd-decorated electrodes, whilst an Ir-coated electrode showed the best electrochemical behaviour.^{13,14} Gonzalez et al. modified GF using nano-dispersed bismuth, and claimed excellent electrochemical performance of the materials in the positive half-cell along with good long-term stability.¹⁵ Similarly, electrodes containing metal oxides, such as Nb₂O₅, Mn₃O₄, and WO₃ were reported as promising candidates for VRFB, particularly due to their low cost.^{16–18} Nb₂O₅, for instance, was proven to have powerful catalytic activity towards both VRFB couples. By contrast, WO₃ showed a limited effect on electrochemical behaviour and Mn₃O₄ was found to be soluble in an acidic environment.

Recently, transition metal nitrides and carbides have attracted increasing interest due to their high stability and good electrical conductivity.^{19–22} For instance, Wei et al. bonded titanium carbide nanoparticles onto carbon paper by means of NafionTM ionomer.²³ Yang et al. deposited titanium nitride nanoparticles onto carbon paper, and reported improvements in electrochemical behaviour at the negative electrode of a VRFB.²⁴ Similarly, Wei et al. employed titanium nanowire-decorated GF in both half-cells and noticed higher electrolyte utilisation and energy efficiency even at a high current density.²⁵

In this study, we propose a novel synthesis method for the preparation of binder-free titanium carbide (TiC) particles on the surface of carbon fibres using titanium tetrafluoride (TiF₄) as the titanium source. GF was impregnated with TiF₄, and TiC particles were formed by a subsequent hydrothermal reaction (TiO₂ as intermediate product) and carbothermal reduction. The method of preparation is inexpensive and yields uniformly distributed TiC particles on the carbon fibre surface, which boost the charge transfer kinetics of the sluggish negative redox couple (V²⁺/V³⁺). As a result, VRFB cells using TiC-GF negative electrodes revealed substantial improvements in energy efficiency and capacity retention.

2 Experimental

2.1 Preparation of TiC-decorated graphite felt

A precursor solution was obtained by mixing TiF₄ and de-ionised (DI) water. A sheet of GF (SIGRACELL GFD 4.6 EA, SGL Carbon GmbH, Meitingen, Germany) was sonicated in ethanol, washed with DI water and finally vacuum-dried at 80 °C before being immersed into the precursor solution. The GF was then transferred to a Teflon-lined autoclave containing the precursor solution, and the hydrothermal reaction was maintained at 180 °C for 14 h. The as-prepared samples were freeze-dried overnight followed by vacuum drying at 60 °C for 14 h. The GF containing TiO₂ nanoparticles were subsequently transferred to a tube furnace for annealing in an Argon atmosphere. The temperature was ramped up from ambient temperature to 1250 °C at a heating rate of 5 °C min⁻¹ and was kept at 1250 °C for 5 h. After cooling, TiC particles could be readily observed on the carbon fibre surface.

2.2 Material characterisation

The morphology and structure of the TiC particles were studied by scanning electron microscopy (FESEM, JEOL Model JSM-7600F) with an acceleration voltage of 5 kV. High resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL JEM-2100 system, operating at an acceleration voltage of 200 kV. X-ray diffractometry (XRD) was performed with a Shimadzu 6000 setup (40 kV, 30 mA) using Cu-K α radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (AXIS SupraTM, Shimadzu Group) was performed with monochromatic Al-K α (1486.71 eV) operating at 15 kV and 5 mA.

2.3 Electrochemical characterisation

Cyclic voltammetry (CV) was performed using a three-electrode setup and a potentiostat (VMP3, BioLogic Science Instruments, France). A piece of the electrode of interest (1 cm x 1 cm) and a graphite current collector compressed in a plastic holder were used as the working electrode. A platinum mesh and a saturated mercury sulphate electrode (SMSE, Hg|Hg₂SO₄|sat. K₂SO₄) served as the counter and reference electrodes respectively. Voltammetric cycling was conducted between -1.3 V and -0.5 V vs SMSE at a scan rate of 1–5 mV s⁻¹. Before measurement, the pristine graphite felt (GF) was immersed in the electrolyte and vacuum was applied in order to remove air trapped inside the felt and imbibe it with electrolyte.

Additionally, electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 100 KHz to 1 mHz with an AC amplitude of 10 mV to compare the charge transfer resistance of the pristine GF and the TiC-modified felt. Both CV and EIS were carried out with a VRFB electrolyte containing 1.6 M V²⁺/V³⁺ in a of 4 M sulphate at 50% state of charge (SOC). Nitrogen purging was maintained during the experiment to create inert conditions. The temperature of the VRFB electrolyte was kept at 24 ± 1 °C throughout the experiments.

2.3 VRFB performance

The VRFB cell performance was investigated using an in-house fabricated flow cell with an active area of 20 cm² (5 cm x 4 cm). The flow frame was made from PVC with flow distribution channels to facilitate the uniform distribution of electrolyte. Pristine GF electrodes were used in the positive half-cell in all tests and the TiC-modified electrodes were investigated in the negative side only. For the assembly of the cell, 0.6 mm thick graphite plates (SIGRACELL[®] TF6, SGL Technic LLC, Valencia, USA) and an anion exchange membrane (Fumasep[®] FAP 450, Fumatech GmbH, Bietigheim-Bissingen, Germany) were used. A commercial VRFB electrolyte (100 mL) with 1.6 M V²⁺/V³⁺ in a total of 4 M sulphate (GFE, Nuremberg, Germany) was used in each tank. The flow rate was kept constant at 60 mL min⁻¹ using peristaltic pumps. A paraffin oil layer was placed on top of the electrolyte surface to prevent aerial oxidation of the electrolyte during cycling. The electrolyte temperature was kept at 24 ± 1 °C throughout the VRFB measurements. The cell cycling study was performed at various current densities ranging from

60 to 100 mA cm⁻² using a battery charger (NEWARE, China, 10 V/10 A). To monitor long term cell performance, galvanostatic 65-cycle tests were carried out at a current density of 80 mA cm⁻². Charge discharge cycling was conducted between clamp voltages of 0.9 V and 1.65 V.

3 Result and discussions

Herein, we report the synthesis method for titanium carbide deposited onto a graphite felt (TiC-GF) as a negative electrode for use in a VRFB. The formation process of the TiC-particles at the carbon fibre surface involves two major steps: hydrothermal reaction and the formation of uniformly distributed TiO₂ particles on the carbon fibre surface and subsequent transformation to TiC particles by carbothermal reaction according to Eq. 1.

The amount of TiC deposited was around 2.5% by weight as determined by EDX measurements (Fig. S1). A schematic diagram representing the overall procedure for the formation of the TiC-GF is illustrated in Fig. 1.

Fig.1 Schematic representation of the synthesis of TiC particles on the surface of a graphite felt: GF (a), TiO₂-decorated GF (b), and TiC-GF (c).

3.1 Characterisation of TiC modified felt

The morphology of the pristine graphite felt (GF) and the TiC-modified felt (TiC-GF) are shown in Fig. 2.

Fig. 2 SEM image for GF (a-b), TiC-GF (c-d) at different magnifications.

As shown in Fig. 2a and 2b, the pristine fibre exhibits a smooth texture typical of PAN-based carbon fibres (average fibre diameter of around 9 μm). Fig. 1c and 1d show the TiC particles at the surface of the TiC-GF. It is observed that the particles are uniformly distributed across the fibre surface. The particle sizes, however, were rather non-uniform. This was most likely caused by the agglomeration of small TiC particles and/or sintering to larger entities. To further examine both the particle size and crystal structure, HRTEM imaging was performed.

HRTEM characterisation at different magnifications confirms the uniform particle distribution and variations in particles sizes (Fig. 3a and 3b). Diffraction and fast-Fourier transform patterns (FFT) of the TiC particles (Fig. 3c and 3d) reveal that the deposited particles possess a high crystallinity with a lattice fringe d-spacing of around 0.25 nm, corresponding to the (111) plane of the cubic-structured TiC.

Fig 3. Typical HRTEM image (a-b), diffraction pattern (c) and fast Fourier transform pattern (FFT) (d) of TiC particle at the carbon fibre surface.

For the characterisation of physical properties, analysis of the chemical structure and oxidation state of the TiC-GF, XRD and XPS were performed. The XRD spectra of GF and Ti-GF are shown in Fig. 4.

Fig. 4. XRD spectra of the GF and TiC-GF.

The diffraction peak located at 25.6° and the other two peaks located at 43.2° and 53.3° are attributed to (002), (100) and (004) facets of graphite. GF showed the three characteristic peaks, whereas TiC-GF exhibited additional diffraction peaks at 35.9° , 41.8° , 60.7° , 72.7° and 76.7° , corresponding to (111), (200), (202), (311) and (222) planes of the TiC cubic phase (JCPDS:96-9506) respectively. XPS analysis revealed the presence of C, Ti and O for the TiC-GF (Fig. S2). High-resolution spectra of Ti and C were deconvoluted using Gaussian-Lorentz fitting to determine the chemical states. Peaks generated by spin-orbital interaction of Ti2p, resulting in the doublet Ti2p_{3/2} and Ti2p_{1/2}, can be seen in Fig. 5a. The multiple peaks obtained after the deconvolution can be assigned to TiC (455.3 eV, Ti2p_{3/2}), TiC (461.3 eV, Ti2p_{1/2}), TiO (456.6 to 457.5 eV) and TiO₂ (487.5 eV). The presence of TiO and TiO₂ is probably partial oxidation in ambient air exposed during sample handling and residual oxygen/water vapour in deposition chamber. Similarly, the narrow spectrum of C1s presented in Fig. 5b shows two peaks, one at 281.9 eV corresponding to the TiC bond and the other at 284.5 eV corresponding to the graphitic carbon.²⁶⁻²⁸

Fig. 5. XPS spectra of TiC-GF (a) Ti-2p spectrum (b) C1s spectrum.

3.2 Electrode characterisation

Fig. 6a and 6b present the CV curves of the V²⁺/V³⁺ redox couple on pristine and TiC-decorated electrodes. The electrochemical parameters obtained are summarised in Table 1.

Fig. 6. CV of GF (a) and TiC-GF (b) at different scan rates, and Nyquist plot with Randles equivalent circuit (c).

The peak potential separation (ΔE_p), peak currents and their ratios (I_a/I_c) were used as figures of merit for the evaluation of the electrocatalytic activity. For the pristine electrode, low oxidation and reduction currents are observed, which reflect the poor reversibility of the electrode towards the V^{2+}/V^{3+} redox couple.

By contrast, the peak potential difference (ΔE_p) at a scan rate of 1 mV s^{-1} for TiC-GF is only 80 mV, which is substantially lower than for GF ($\Delta E_p=190 \text{ mV}$). Similarly, the peak current ratio is lower for TiC-GF ($I_a/I_c = 1.03$) compared with GF ($I_a/I_c = 1.25$). The dramatic increase in peak current and decrease in peak separation both furnish evidence for the substantially higher reversibility of the TiC-decorated electrode. Fig. S3 shows a linear relationship between the anodic and cathodic peak current and the square root of the scan rate, indicating that the redox reaction is limited by the diffusion within the given scan rate range. The slope for TiC-GF is larger than that of GF, which reflects the presence of a higher number of active sites.^{9, 29}

Table 1. Electrochemical parameter obtained from GF and TiC-GF electrode at different scan rates.

Scan rate (mV s^{-1})	GF		TiC-GF	
	ΔE_p (V)	I_a/I_c	ΔE_p (V)	I_a/I_c
5	0.41	1.06	0.22	1.03
3	0.34	1.03	0.16	1.02
2	0.28	1.04	0.13	1.02
1	0.19	1.25	0.08	1.03

Figure 6 shows the results from EIS (Nyquist plot and the corresponding equivalent circuit used for fitting). With the introduction of TiC, the charge transfer resistance is decreased to 0.31Ω . This is significantly lower as compared to pristine GF (3.19Ω) and is highly consistent with the CV results.

3.3 Single cell tests

Typical charge/discharge tests were performed using VRFB single cells to demonstrate the practical application of TiC-GF. Identical cells with GF and TiC-GF at the negative electrodes were assembled with a felt compression of 24%. The dry cell resistance was the same for both cells (approx. $0.15 \Omega \text{ cm}^2$), which clearly indicates that the modification has no noticeable effect on the (bulk) electronic conductivity. Stated otherwise, differences in cell performance will be related to electrode kinetics. Energy efficiency and voltage efficiency from 60 to 100 mA cm^{-2} are plotted in Fig. 7a and 7b.

At a current density of 100 mA cm^{-2} , a gain in energy efficiency of 13% was observed by using a TiC-GF negative electrode instead of a virgin GF. A comparison of the voltage profile vs specific capacity (Ah L^{-1}) at a current density of 80 mA cm^{-2} is shown in Fig 7c. For the TiC-GF, significant shifts in the charge (-100 mV) and discharge ($+170 \text{ mV}$) curves as compared to cells containing pristine GF as negative electrodes were observed.

Under fixed cut-off voltages between 0.9 V to 1.65 V, the use of pristine GF negative electrode resulted in a relatively poor specific capacity of 4.3 Ah L^{-1} , which reflects the poor utilisation of electrolyte. With the introduction of TiC particles at the negative electrode, the specific capacity increased to 6.4 Ah L^{-1} (48% higher than that of GF). The TiC-GF exhibits a low charging voltage plateau and a high discharging plateau, signifying lower charging and higher discharging voltage. This leads to a higher charge/discharge capacity within a given voltage window. It can also be assumed that the faster charge-transfer kinetics of the negative couple are accompanied by the suppression of the hydrogen evolution reaction (HER), which occurs as a parasitic side reaction at the negative electrode.

Hence, the improved electrochemical properties of the TiC-GF can be unequivocally attributed to the presence of electronically conductive and catalytically active particles. Moreover, the nanometer-size particles generate a significantly higher surface area. Both effects contribute to the substantially higher reversibility of the V^{2+}/V^{3+} reaction at the TiC-GF electrode.

Fig. 7d shows the area-specific resistance (ASR) at different current density levels. The ASR represents the average wet cell resistance of the cell during charging and discharging. The average ASR (R_a) during charging/discharging is calculated by the formula given below:

$$R_a = \frac{V_{oc}}{j_{app}} \cdot \frac{(1-VE)}{(1+VE)} \quad (2)$$

Where j_{app} is the applied current density, VE is the voltage efficiency and V_{oc} is the average open-circuit voltage during charge and discharge ($\sim 1.38 \text{ V}$ at 25°C). The use of the TiC-GF as the negative electrode reduces the ASR by about 40%, which contributes to an effective utilisation of the electrolyte capacity. Catalyst stability during long-term operation is one of the critical issues for its use in the VRFB, as the catalyst needs to withstand the corrosive environment of the electrolyte and should not be flushed away by the flowing electrolyte. In order to test the stability of the TiC-GF, 65 consecutive charge-discharge cycles were run at a current density of 80 mA cm^{-2} . Fig. 8a and 8b show the corresponding energy efficiency and discharge capacity of the pristine and TiC-GF. The TiC-GF adds 13% to the energy efficiency as compared to GF. The small drop in efficiency during cycling is caused by a net electrolyte transfer from the positive to the negative tank, which is commonly observed when using anion exchange membranes. Similarly, the discharge capacity of the VRFB with a TiC-GF shows 84% of the initial capacity after 65 cycles with a capacity decay of 3.33 mAh per cycle. By contrast, the cell using the pristine GF as the negative electrode maintained only 70% of the initial capacity after 65 cycles and the capacity loss is also significantly higher (around 5.3 mAh per cycle). This once again highlights the excellent stability and electrochemical performance of a TiC-GF negative electrode.

Fig. 7. Comparison of energy efficiency (a), voltage efficiency (b), specific capacity at 80 mA cm⁻² (c) and area specific resistance (d) of GF and TiC-GF.

Fig. 8. Cycling test of VRFBs: energy efficiency (a) and discharge capacity (b), at current density of 80 mA cm⁻² with GF and TiC-GF.

In summary, the investigations verified that the use of GF containing TiC nanoparticles as the negative electrode in VRFB increases the overall efficiency of the VRFB. This increase in performance is solely attributable to the enhanced reversibility of the TiC-GF negative electrode. A possible mechanism of the catalytic effect of TiC particles is proposed in Figure 9, based on the early study conducted by Skyllas-Kazacos *et al.*⁸ Initially, ion exchange occurs between the hydrogen ion of TiC-O-H and a V^{2+} during charging and V^{3+} is absorbed to the Ti-C-O-H layer. Secondly, V^{3+} are reduced to V^{2+} as electrons transfer from Ti-C-V(II) complex to Ti-C-V(I). Finally, the V(I) complex turns to V^{2+} (desorption process). During discharge, the reaction occurs in opposite direction.

Fig. 9. Proposed mechanism of V^{2+}/V^{3+} redox reaction in the presence of TiC particles.

4 Conclusions

A novel method for the preparation of titanium carbide nanoparticles supported on graphite felts for use in vanadium redox flow batteries is presented. Our approach involves hydrothermal conversion of a TiF_4 precursor adsorbed onto carbon fibre surfaces to TiO_2 , followed by a carbothermal reduction of TiO_2 particles to TiC. Electrochemical tests of the materials as negative electrodes showed significant gains in overall VRFB cell performance which were attributed to the catalytic effects of TiC particles on the surface of the graphite felt. Energy efficiency and electrolyte utilisation increased considerably as compared to the cells using pristine felt electrodes. The TiC-decorated electrode exhibited excellent stability and capacity retention over repetitive cycling. These findings suggest that our approach constitutes a viable concept for high performance negative electrodes for vanadium redox flow batteries.

Conflicts of interest

There are no conflicts to declare.

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