Carbon Felt Coated with Titanium Dioxide/Carbon Black Composite as Negative Electrode for Vanadium Redox Flow Battery

Tung-Mo Tseng, a,b Rong-Hsin Huang, a,b Chung-Yen Huang, a Chung-Chiu Liu, b,* Kan-Lin Hsueh, a,** and Fuh-Sheng Shieu a,**

aDepartment of Materials Science and Engineering, National Chung Hsing University, Taichung 40227, Taiwan
bDepartment of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106, USA

This investigation focuses on the effect of titanium dioxide (TiO2) coatings of a carbon black (XC-72) negative electrode on the performance of a vanadium redox flow battery (VRFB). TiO2, a hydrophilic material, was added to the carbon electrode to improve the wettability and reduce the electrical resistance of the electrode surface. The electrochemical performances of homemade TiO2, commercial TiO2, and carbon felt are investigated by using cyclic voltammetry and single-cell charge–discharge measurements.

At current density of 200 mA cm\(^{-2}\), the energy storage efficiency (\(\eta_E\)) of the single cell with 20 wt% of a TiO2/C-containing carbon felt negative electrode is 16.0% and 6.1% higher than that of the negative electrode with raw carbon felt (\(\eta_E = 56.4\%\)) and of the negative electrode containing commercial TiO2/C (\(\eta_E = 61.6\%\), respectively).

These results demonstrate the potential application of TiO2/C electrodes for high-efficiency VRFBs at high current densities.

Vanadium redox flow battery (VRFB) has been proposed as a promising candidate for large scale energy storage applications, such as load-leveling applications. VRFB can store and stabilize intermittent electricity generated from wind turbine or photovoltaic. VRFB has several advantages over other types of batteries, such as excellent electrochemical reversibility, high roundtrip efficiency, flexible, and negligible cross-contamination between positive and negative electrolytes.1,5 VRFB employs V(IV)/V(V) and V(II)/V(III) redox couples as positive and negative half-cells, respectively, with the standard open circuit cell potential approximate 1.26 V at 100% state of charge.6

Carbon felt is a typical electrode material and it has wide operating electrode potential range, chemically stable, high surface area, and reasonable price. However, carbon felt electrode shows poor electrochemical activity. Therefore, much attention has been focused to electrode modification to enhance its electrochemical properties.7–14

Several alternative electrode materials have been proposed to improve electrode performance, such as metal electrodeposition on carbon fibers. Various metal compounds have also been deposited on graphite fibers to improve the catalytic activity for vanadium redox couples and to enhance electrode stability in acidic vanadium solution. In the literature, metal compounds deposited on carbon felt include IrO2,5 RuO2,10 and Ir,11 whereas others include partial modification of the functional groups on the graphite surface.12,13 The coating of metal nanoparticles on the fiber of carbon felt is a promising approach. Recently, transition metal oxides, e.g., TiO2, ZnO, have been studied extensively as a water absorbent for improving the wettability of the catalyst layer, thus the performance of proton exchange membrane fuel cell14,15 was enhanced. Besides, TiO2 has satisfactory chemical stability, endurance, and lower production costs.16 The property of TiO2 is influenced by crystal structure, surface area, size distribution, porosity, bandgap, and surface hydroxyl density.17,18 Titanium dioxide mixed with carbon black has been proven19 to be a good electrode additive for VRFB application at a low current density of 20 mA cm\(^{-2}\). The study of TiO2 as an additive for the VRFB electrode at high current density is rarely discussed in literature. Our previous study19 indicated that addition of TiO2 powder on the VRFB electrode can enhance cell performance. Nevertheless, the current density tested in our previous study was far lower than that required for practical applications. Therefore, this study intends to explore the feasibility of adding TiO2 on the electrode at much higher current density (200 mA cm\(^{-2}\)) than 20 mA cm\(^{-2}\).

At high current density such as 200 mA cm\(^{-2}\), numerous side reactions or problems may be encountered. In long-term VRFB operation, gas evolution may occur on the electrodes during the battery charging period. Gas evolutions (both hydrogen and oxygen evolution reactions) result in the loss of energy efficiency and storage capacity.20 This study aims to evaluate the effects of hygroscopic titanium dioxide (TiO2) nanoparticle deposited onto a carbon black negative electrode on the performance of a vanadium redox flow battery (VRFB) at high current density. Charge–discharge measurement was conducted under ambient conditions. Electrode material containing various TiO2 amounts was loaded onto the carbon black (XC-72) composite. This study aims to find the preparation condition of the electrode containing TiO2 and the electrochemical performance of the electrode for VRFB.

Experimental

The experimental conditions, procedure, and instruments used in this study are described in detail in the following sections.

Preparation of anatase TiO2 particles and TiO2/C composite electrode.— A two-step sol-gel process (hydrolysis, condensation, and calcination) in basic medium was used to synthesize anatase TiO2 particles from the precursor, tetra-n-butyl titanate (TnBT, Alfa Aesar). The hydrolysis process was carried out in an ice-water bath. The TnBT (0.05 mol) dissolved in 20 mL ethylene glycol (EG, Aldrich), was added to the mixture of water and ethylene glycol (\(V_{\text{water}}/V_{\text{EG}} = 1/1\), \(V_{\text{max}} = 20\) mL). This mixture was magnetically stirred to yield a 40 mL solution. Subsequently, the solution was thermostated and cooled in an open vessel. The solution temperature was gradually increased to 103°C for 6 h to remove the solvent by evaporation. It was then dried at 120°C for 10 h to remove the by-product, butyl alcohol. The precursor was washed by centrifugation/re-dispersion cycles with ethanol and water to remove residual EG. The precipitate was then dried in a vacuum oven at 300°C overnight. The TiO2/C composite electrodes were prepared by mixing TiO2 particles and carbon black with 20 wt% fabricated TiO2 loading at a scan rate of 0.006 V s\(^{-1}\) shows a specific capacitance (\(C_s\)) of 186.2 F g\(^{-1}\), which is 55.5% and 12.2% higher than that of pure carbon electrode (119.7 F g\(^{-1}\)) and commercial TiO2 (166.0 F g\(^{-1}\)) respectively. At current density of 200 mA cm\(^{-2}\), the energy storage efficiency (\(\eta_E\)) is 65.4% of the single cell with 20 wt% TiO2/C-containing carbon felt negative electrode is 16.0% and 6.1% higher than that of the negative electrode with raw carbon felt (\(\eta_E = 56.4\%\)) and of the negative electrode containing commercial TiO2/C (\(\eta_E = 61.6\%\)), respectively.

This study aims to find the preparation condition of the electrode containing TiO2 and the electrochemical performance of the electrode for VRFB.

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(Vulcan XC-72). The TiO2/C composite electrodes were prepared by mixing TiO2 particles and carbon black (Vulcan XC-72). The mixing was carried out using the thermal-reflux method. First, well-mixed suspension of carbon black was obtained by adding 0.8 g of carbon black and 30 mL of ethanol under ultrasonication for 4 h. Afterward, 0.2 g of TiO2 and 20 mL of deionized water were added to the carbon black ink under ultrasonication for another 4 h. A 1.0 M NaOH solution was gradually added to the mixture until the pH reached 10 to 11. Finally, the mixed ink (TiO2/C ink) was constantly stirred under thermal reflux at 80 °C for 4 h. The 20 wt% TiO2/C powder was filtered and dried overnight at 90 °C in a vacuum oven. The weight ratios of the homemade TiO2/XC-72 (HM-TOC-20) and commercial-TiO2/carbon (COM-TOC-20) were both 20 wt%.

Material characterization analysis.— The crystal structure of the carbon black (Vulcan XC-72), commercial TiO2 (Biocare, USA), and homemade-TiO2 (HM-TiO2) were analyzed by X-ray diffraction (XRD, Rigaku D/MAX 2500) with Cu Kα radiation (λ = 1.5418 Å). The XRD diffraction spectra were recorded in the range from 20° to 70° (2θ) at a scan rate of 2° min−1 and the result was compared with the JCPS data files. High-resolution field-emission transmission electron microscopy (HR-TEM, JEOL Model JEM-2100F) operated at 200 kV was used to examine the size, morphology, and distribution of the TiO2/C composition material. The TiO2/C sample for TEM analysis was prepared by the following procedure and condition. The commercial-TiO2 and homemade-TiO2 inks were placed in a vial containing ethanol and then ultrasonically agitated until the inks became homogeneous. A drop of the inks was spread on a holey copper grid for TEM observation. The size distribution of the anatase TiO2 nanoparticles in TiO2/C electrode material was obtained by directly measuring 300 randomly selected TiO2 particles from the TEM images. The sessile drop method (First Ten Angstro, FTA 2000, USA) was used to measure the water contact angle of the TiO2/C composite electrodes. TiO2/C ink was sprayed onto one side of commercial hydrophobic carbon felt, and then dried at 60 °C for 30 min. Each sample was measured five times at different locations, and the average water contact angle was then calculated.

Electrochemical characterization techniques: cyclic voltammetry and charge-discharge tests.—The electrochemical characteristics of the TiO2/C composite electrodes were evaluated by cyclic voltammetry (CV), CHI Instruments (Model 614B, USA) with a three-electrode cell. The TiO2/C composite ink (1.25 mg TiO2/C + 50 μL of 5 wt% Nafion solution) was coated on the working electrode for electrochemical measurements. The working electrode was a glassy-carbon electrode with a geometric surface area of 0.196 cm2. Pure Pt wire was used as the counter electrode, whereas a saturated Ag/AgCl was used as the reference electrode. During CV, the electrode potential was first scanned toward the positive direction. The potential scanning rate was varied from 0.002 V·s−1 to 0.006 V·s−1 in a 1.0 M H2SO4 (Aldrich, 98.5%) solution.

A single cell was used for the battery charging/discharging experiment. Nafion 117 (DuPont), a proton-exchange membrane, was used as separator. Commercial raw carbon felt, with dimensions of 5.0 × 0.5 × 0.6 cm3 (Carbon Felt-CF060A01836, CeTech Co., Ltd.), served as the base of the positive and negative active electrodes, as shown in Fig. 1. The Nafion 117 membrane [(7.0 × 7.0) cm2] was pretreated with 5 wt% H2O2 (Aldrich), deionized water, 1.0 M H2SO4 (98.5%; Aldrich), and deionized water at 80 °C for 1 h. Each graphite plate (Beam Associate Co., Ltd.) was filled with an equal size of raw carbon felt (fillister dimensions of 5.0 × 5.0 × 0.6 cm3). A constant-current charge–discharge test was performed using a single-cell testing system (Beam Associate Co., Ltd.). The positive electrode was a raw carbon felt with an area of 25 cm2 (5.0 cm × 5.0 cm), while the negative electrode was TiO2/C-modified carbon felt.

The negative electrode was prepared by following procedure: a mixture of TiO2/C composite electrode ink was prepared by adding TiO2/C nanoparticles, 5 wt% Nafion solution (DuPont, USA), and alcohol (98%; Aldrich), and subsequent ultrasonication the mixture for 1 h. TiO2/C ink, which serves as the activation layer of the composite electrode, was sprayed onto the raw carbon felt and then dried at 65 °C for 6 h in a vacuum oven at a pressure of 1.013 × 10−3 Pa. This drying process resulted in a deposition of the TiO2/C particles on the raw carbon felt. The charge–discharge test was performed using a potentialstat/galvanostat instrument (263A, EG&G, USA) at lower and upper charge voltage limits of 0.8 and 1.9 V, respectively, under around 25 °C in an air-conditioned lab. The input flow rates of electrolyte in both electrodes were maintained at 30 mL min−1 by using a peristaltic pump (P10–100, Firstek Sci. Co., Ltd.). The solution for this experiment comprised 3.0 M V(IV) and 2.0 M H2SO4, which was prepared by dissolving 489.0 g of VOSO4•3H2O in H2SO4 solution (total volume = 1.0 L; the solution contained 200 g of 98.5% concentrated H2SO4). The initial solution in the cell was 3.0 M V(IV) + 2.0 M H2SO4 in both compartments. However, a 130 mL solution was placed in the positive compartment and a 65 mL solution was placed in the negative compartment. The cell was initially charged to its full capacity. The V(IV) in the positive compartment was converted into V(V), whereas the V(IV) in the negative compartment was converted into V(II). After the initial charge, the 65 mL solution in the positive compartment was removed. The electrolyte volumes in both compartments are equal at 65 mL. The performance of the V(V)/V(IV) cell was tested under ambient conditions at a constant current density of 200 mA cm−2 in both charge and discharge cycles. The input flow rates of the electrolyte in both electrodes were maintained at 30 mL min−1 using a peristaltic pump.

It is also evaluated to understand the effects of vanadium ion concentration on the charge–discharge performance of a single cell at 200 mA cm−2. The electrolyte composition is listed in Table II.

Results and Discussion

Material analysis.—Figure 2 displays the wide angle diffraction (XRD) spectra of HM-TiO2/C, HM-TiO2, and commercial-TiO2 particles. The diffraction peaks at 25.8°, 38.8°, 48.0°, 53.9°, 55.0°, and 62.7° are consistent with the anatase titanium dioxide phase. The broad peak near 25° is attributed to carbon black. Figure 3a shows that the HM-TiO2 nanoparticles were well-dispersed on the carbon black (Vulcan XC-72) surface. The histogram of the samples is inserted in Figs. 3a and 3c. The average particle sizes of HM-TiO2 and commercial-TiO2 were approximately 9.1 ± 2.0 nm and 16.1 ± 1.2 nm, respectively. A typical high-resolution TEM image, as shown in Fig. 3b and Fig. 3d, reveals the highly crystallized TiO2 nanocrystal with a lattice spacing of 0.35 nm, which corresponds to the (101) plane of anatase TiO2.

The hydrophilic characteristic of the TiO2/C composite electrode was investigated by a sessile drop method. Figure 4 shows the water contact angle images of carbon black (XC-72, CB), commercial TiO2, and HM-TiO2, which are 132°, 88°, and 52°, respectively. The contact angle of the electrode layer containing TiO2 nanoparticles is
significantly lower than that of the electrode without TiO₂. Therefore, the wettability of the nanoparticle electrode layer containing TiO₂ is better than that of the electrode without TiO₂.

Electrochemical characterization of TiO₂/C composite material.— Figure 5 shows the cyclic voltammograms of Vulcan XC-72, COM-TOC-20, and HM-TOC-20 composite electrodes in 1.0 M H₂SO₄ solution at a scan rate of 0.006 V s⁻¹. At −0.4 V against Ag/AgCl, the TOC composite electrodes exhibit a higher double-layer charging current than XC-72. The oxidation-reduction current within the potential range of −0.4 V to −0.5 V was due to hydrogen adsorption/evolution reaction. The hydrogen reduction peak was not clearly observed in this cyclic voltammogram. Therefore, only the oxidation current was used to evaluate the electrochemical surface area or activity of the electrodes. Results suggest that the composite electrodes have higher specific capacitance and higher electrochemical active area than that of the XC-72 electrode.

In the potential region between −0.5 and −0.4 V, the specific capacitance of the composite electrodes is a combination of double-layer capacitance and faradaic pseudo-capacitance attributed to hydrogen adsorption/desorption. The current detected in the potential range from −0.4 to −0.3 V is mainly attributed to double-layer charging-discharging current. The specific capacitance (C₁,t) of the composite electrodes can be roughly calculated from the current measured in this potential region, which was calculated by using from the following equation:

\[ C_{s,t} = \frac{I_a + |I_c|}{2W\left(\frac{dV}{dt}\right)} \]  

where \( I_a \) and \( I_c \) are the currents of anodic current and cathodic current at −0.40 V, respectively; \( W \) is the mass of the composites (in grams); and \( dV/dt \) is the scan rate (in volts per second). Figures 6a to 6c show the CVs of XC-72, COM-TOC-20, and HM-TOC-20 at different scanning rates. Table I lists the values of specific capacitance (\( C_{s,t} \)) calculated from Eq. 1 and the TiO₂ loading of each sample. In general, \( C_{s,t} \) increases with the increase in TiO₂ loading. The \( C_{s,t} \) value of pure XC-72 and HM-TOC-20 are 119.7 and 186.2 F g⁻¹, respectively. Addition of TiO₂ in the electrode reduced the contact angle between water and electrode, as shown in Fig. 4. This finding suggests that addition of TiO₂ increases the effective electrode area (hydrophilic area inside electrode), which is also evidenced by the results of specific capacity measurement. With the same amount of TiO₂ added on the electrode, the \( C_{s,t} \) of COM-TOC-20 was 166.0 F g⁻¹, which was less...
Figure 4. Results of contact angle measurement using water droplets on carbon XC-72 power with (a) 0 wt% of TiO2, (b) 20 wt% of commercial-TiO2, and (c) 20 wt% of HM-TiO2 addition on the carbon felt.

Figure 5. Cyclic voltammograms of electrode materials: (a) carbon Vulcan XC-72, (b) COM-TOC-20, and (c) HM-TOC-20 in 1.0 M H2SO4 solution at a sweep rate of 0.006 V s\(^{-1}\).

Figure 6. Cyclic voltammograms of electrode materials: (a) carbon Vulcan XC-72, (b) COM-TOC-20, and (c) HM-TOC-20 under different scan rates in 1.0M H2SO4 solution.

than that of HM-TOC-20. The loss of the double-layer capacitance of COM-TOC-20 can be attributed to the aggregation of TiO2 particles, as demonstrated by the TEM micrograph in Fig. 3 (16.1 nm for COM-TOC-20 and 9.1 nm for HM-TOC-20).

Pores on the Vulcan XC-72 surface are generally hydrophobic and are inaccessible for aqueous solution and ion transport. Therefore, hydrophobic pores are both inaccessible for ions and electrochemically inactive.\(^{25}\) The introduction of hydrophilic TiO2 produces faradaic pseudo-capacitance. Vulcan XC-72 has a high specific area and excellent conductivity. Addition of hydrophilic TiO2 further improves the hydrophilic property and the double-layer capacitance of the mixture of TiO2 and Vulcan XC-72. Figure 7 presents the relationship between the specific capacitance and the potential scanning rate of different composite electrodes. The figure shows that the composite electrode has higher specific capacitance than that of Vulcan XC-72. The specific capacitance of a given sample is independent of the scanning rate. The optimal TiO2 loading is approximately 20 wt% in this study.
Table I. Specific capacitances of titanium dioxide/XC-72 composite with different contents.

| Electrode | TiO₂ Loadings (mg cm⁻²) | Capacitances of composite electrodes at different scan rates (F g⁻¹) |
|-----------|--------------------------|------------------------------------------------------------------|
| XC-72     | 0.000                    | 0.002 V s⁻¹ 112.7 0.004 V s⁻¹ 121.2 0.006 V s⁻¹ 119.7            |
| COM-TOC-20| 0.058                    | 0.002 V s⁻¹ 169.5 0.004 V s⁻¹ 167.5 0.006 V s⁻¹ 166.0            |
| HM-TOC-20 | 0.058                    | 0.002 V s⁻¹ 191.3 0.004 V s⁻¹ 189.6 0.006 V s⁻¹ 186.2            |

Charge–discharge test.— Our previous study¹⁹ indicates that H₂ evolution occurs more easily in raw carbon electrode than in acidic- or thermal-treated carbon electrode. The CV at potential < −0.5 V against Ag/AgCl, as shown on Fig. 8, confirmed that H₂ evolution easily occurred in the raw carbon felt electrode in the V²⁺/V³⁺ redox reaction. After adding TiO₂, H₂ evolution reaction rate is suppressed. Addition of TiO₂ enhances the hydrophilic ability of carbon felt and the electrochemically active area of composite electrode is increased, as indicated by the hydrogen adsorption/desorption peaks in Fig. 8. As a result, the hydrophilic TiO₂ was added to the negative electrode in subsequent experiments to prevent H₂ evolution.

A single cell with four different electrode materials was analyzed to determine the effect of TiO₂/C-modified felt on charge-discharge performance. Raw felt was used as positive electrode for all cells tested. The negative electrode of cell A used raw felt, whereas COM-TOC-20 and HM-TOC-20-modified felt served as the negative electrodes for cells B and C, respectively. The thickness of all electrodes was 6 mm. We investigated the effect of electrolyte composition on the charge–discharge curves, as given in Fig. 9a. Electrolytes with three different compositions were tested, and their compositions were listed in Table II. The cutoff voltage during charging was 1.9 V, and the cutoff voltage during discharge was 0.8 V. Both the charging and discharging times were increased as the vanadium concentration in the solution increased, as shown in Fig. 9a. The voltage drop when current switched from charge to discharge was decreased as the vanadium concentration increased, and the theoretical capacities calculated from the vanadium concentration were listed in Table II.

Both capacities measured from Fig. 8a and from the theoretical calculation are listed in Table II. As an example, the theoretical and experimental capacities of solution 3 were 5226 mAh and 3976 mAh, respectively. The 3976 mAh was calculated from Fig. 9a, 5000 mA × 2863 s × 3600⁻¹ s = 3976 mAh. Experimental capacities depend linearly on vanadium concentration. The ratio of the experimental capacity to the theoretical capacity is also listed on the same Table II. The concentrated solution (solution 3) had the highest ratio among three solutions tested. This result may be attributed the fact that the cell was not fully charged. To avoid possible water electrolysis during the charge period, the upper limit of cell voltage during charge was set at 1.9 V. At fixed current density and electrolyte flow rate, high
Table II. Theoretical capacity of cell A with different electrolyte compositions under charge–discharge at 200 mA cm\(^{-2}\).

| Solution | Composition \(^a\) | Theoretical capacity (mAh) | Experimental capacity (mAh) | Capacity ratio |
|----------|-----------------|---------------------------|----------------------------|---------------|
| 1        | 1.0 M V(IV)/ 1.0 M V(III) in 2.0 M H\(_2\)SO\(_4\) | 1742 | 691 | 39.7% |
| 2        | 2.0 M V(IV)/ 2.0 M V(III) in 2.0 M H\(_2\)SO\(_4\) | 3484 | 2152 | 61.8% |
| 3        | 3.0 M V(IV)/ 3.0 M V(III) in 2.0 M H\(_2\)SO\(_4\) | 5226 | 3976 | 76.1% |

\(^a\)Solution composition: Anode V(IV) concentration/Cathode V(III) concentration

Table III. Electrochemical performance of cell efficiency values for cells A, B, and C at a charge–discharge current density of 200 mA cm\(^{-2}\).

| Cycle | Coulombic efficiency (\(\eta_C\)) | Voltage efficiency (\(\eta_V\)) | Energy efficiency (\(\eta_E\)) |
|-------|---------------------------------|-------------------------------|-------------------------------|
|       | A | B | C | A | B | C | A | B | C | A | B | C |
| 1     | 83.5% | 86.4% | 88.6% | 66.2% | 70.1% | 72.8% | 55.3% | 60.5% | 64.1% |
| 2     | 85.2% | 87.7% | 90.1% | 66.3% | 70.2% | 73.0% | 56.4% | 61.6% | 65.3% |
| 3     | 87.2% | 89.8% | 91.5% | 66.3% | 70.2% | 73.1% | 57.5% | 62.8% | 66.8% |
| Averaged efficiency | 85.4% | 87.9% | 90.0% | 66.3% | 70.2% | 73.0% | 56.4% | 61.6% | 65.4% |

Figure 10. Charge/discharge curves of single cell with different negative electrode materials: (a) Cell A–raw carbon felt, (b) Cell B–COM-TOC-20 + carbon felt, and (c) Cell C–HM-TOC-20 + carbon felt. Raw carbon felt was used at the positive electrode, and testing was performed at a charge–discharge current density of 200 mA cm\(^{-2}\).

Concentration over-potential is expected for cells containing low vanadium concentration. At 1.9 V, the state of charge (SOC) of the cells containing low vanadium concentration is lower than that containing high vanadium concentration.

Figure 9b represents the charge–discharge curves of cells at a constant current density of 200 mA cm\(^{-2}\). An abrupt cell voltage drop was detected when the current was reversed from charge to discharge. Cell internal resistance \(R\) (in ohm cm\(^{-2}\)) can be estimated from the cell voltage drop during current switching from charge to discharge (Fig. 9b). The IR drop of the different electrodes follows the order: cell C (0.56 V) < cell B (0.60 V) < cell A (0.64 V), as shown in Fig. 9b (curves A to C at 200 mA cm\(^{-2}\)). Internal resistance values calculated from Eq. 2 are in the order of cell C (1.4 \(\Omega\) cm\(^{-2}\)) < cell B (1.5 \(\Omega\) cm\(^{-2}\)) < cell A (1.6 \(\Omega\) cm\(^{-2}\)), as shown in Fig. 9b (curves A to C at 200 mA cm\(^{-2}\)).

\[ R = \frac{V_C + V_D}{2I} \times A \]
Conclusions

Spherical TiO$_2$ nanoparticles of average size 9.1 ± 2.0 nm were successfully prepared by using a sol-gel method. The homemade TiO$_2$ exhibited excellent hydrophilicity, by which the water contact angle of the 20 wt% HM-TiO$_2$ nanoparticles (52°) is smaller than that of the 20 wt% commercial TiO$_2$ nanoparticles (88°) and the carbon black XC-72 (132°). The single cell where negative electrode containing hydrophilic TiO$_2$ nanoparticles had larger electrochemical active area, lower internal resistance, higher specific capacitance, and energy storage efficiency than the single cell where negative electrode containing commercial TiO$_2$ nanoparticles or without TiO$_2$ nanoparticles. A 90% coulomb efficiency, 73% voltage efficiency, and 65.3% energy efficiency could be achieved at 200 mA cm$^{-2}$ with electrolyte containing 3 M V(V)/V(III), 2.0 M H$_2$SO$_4$.

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