COMMUNICATION

Black Pearls Carbon as Catalyst for All-Vanadium Redox Flow Batteries

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

DOI: 10.1039/x0xx00000x

Supplementary Information

Experimental

Black Pearls 2000 Carbon Black, Cabot Corporation, MA, USA (BET 1588 $m^2 \cdot g^{-1}$, pore volume 2.2 $cm^3 \cdot g^{-1}$, pore diameter 5.4 nm). Acetylene Carbon Black (ACB), Alfa Aesar, MA, USA (BET 82 $m^2 \cdot g^{-1}$, pore volume 0.3 $cm^3 \cdot g^{-1}$, pore diameter 14.4 nm). Multi-walled Carbon Nanotubes (MWCNTs), made in-house (BET 139 $m^2 \cdot g^{-1}$, pore volume 0.6 $cm^3 \cdot g^{-1}$, pore diameter 16.8 nm), the method of preparation can be obtained from the work of Fard et al. [1]. Graphene Nanoplatelets (GNP), provided by IREC in Spain with (BET 295 $m^2 \cdot g^{-1}$, pore volume 0.2 $cm^3 \cdot g^{-1}$, pore diameter 1.9 nm). Vulcan Carbon XC-72R (BET 245 $m^2 \cdot g^{-1}$, pore volume 0.5 $cm^3 \cdot g^{-1}$, pore diameter 7.7 nm), 4" by 4" by 0.125" Isomolded graphite plates and 50 µm thick Nafion™ membrane (N212) were purchased from Fuel Cell Store, USA. All carbon materials reported in this work were used as-received and/or as-prepared in the case of MWCNTs.

The single cell battery was built in-house with serpentine flow channels of 1.6 mm and 1.33 mm channel depth and width, respectively and 3.4 cm by 3.4 cm active area. Nafion™ membrane (N212), sandwiched between two carbon paper electrodes (200 µm thick) was used to form membrane electrode assembly (MEA). On the anode, Toray or Toray-coated carbon paper electrode was used while on the cathode, a commercial vanadium-redox-active carbon paper (name withheld) electrode was used.

All the redox and water-based chemicals used in this work were prepared with deionized water (18.20 MΩ.cm^{-1}). $VOSO_4$ as a reagent grade, H_2SO_4 with assay 99.999% and 5 wt.% Nafion™ solution were purchased from Sigma Aldrich.

To investigate V-redox reactions on different carbon electrodes, three-electrode cell was used with 0.1 M $VOSO_4$ in 2 M H_2SO_4.

As for Cell performance, 1.5 M $VOSO_4$ in 2 M H_2SO_4 was used in both anolyte and catholyte. It is important to mention that since the starting material is $VOSO_4$ with Vanadium ions having a charge state of +4, the initial battery charge cycle was performed to balance the charge of vanadium species; in other words to generate V^{+2} and VO_2^+ on anode and cathode side, respectively.

Ink Formation of BP carbon

(i) About 5 mg of each carbon was dispersed with 10 wt.% of Nafion™ solution (binder) in a mixture of 7 ml of deionized water and 3 ml of Isopropyl alcohol (IPA). In each case, the mixture was sonicated for at least 10 minutes to attain homogeneity.

(ii) For BP-coated carbon paper, about 294 mg of carbon powder mixed with 10 wt.% of Nafion™ solution (binder) was dispersed in 21 ml of deionized water and 9ml of Isopropyl alcohol (IPA) and sonicated for 10 minutes to attain homogeneity. The prepared ink was sprayed onto a known dimension of Toray carbon paper substrate, and then dried in an oven at 60 °C for 2 hours. Based on weight gain, the loading of BP on Toray carbon substrate was estimated to be 0.12 $mg \cdot cm^{-2}$. This was repeated for MWCNTs- and GNP-coated Toray carbon papers.

Electrochemical Characterization

To investigate cyclic voltammetry behavior of the different carbon materials, thin-film electrodes were prepared on a glassy carbon disk (6.5 mm diameter). 20 µl of the ink was carefully deposited (with pipette) onto the glassy carbon disk and allowed to dry. The disk holder was mounted on a rotating ring-disc electrode (RRDE), dipped into 50 ml of prepared redox electrolyte (0.1 M $VOSO_4$ in 2 M H_2SO_4) in a 3-electrode jacketed cell. The disk acted as the working electrode, Ag-AgCl (red-rod) as the reference electrode and highly porous graphite rod as the counter electrode.

As for cyclic voltammetry of BP-coated Toray carbon paper, a small piece (0.32 cm^2) of the coated carbon paper was cut and mounted on an in-house made graphite rod holder and dipped

[a] *Address here.*
[b] *Address here.*
[c] *Address here.*
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

into same aforementioned cell containing 0.1 M $VOSO_4$ in 2 M H_2SO_4. The cyclic voltammetry of the thin-film was carried out with WaveDriver 20 Bipotential/Galvanostat (Pine Research Instrument, USA). 10 $mV \cdot s^{-1}$ scan rate was used for both single scan and for durability test involving hundreds of cycles. For cell performance measurements, SP-300 Potentiostat/Galvanostat (BioLogic Science Instruments, France) was used. The cell was run on constant current chronopotentiometry using EC-Lab (in-built software) at 35 $mA \cdot cm^{-2}$ current density.

1. A. K. Fard, G. Mckay, Y. Manawi, Z. Malaibari and M. A. Hussien, *Chemosphere*, 2016, **164**, 142-155.