Supporting Information

Fullerene C_{76} as a novel electrocatalyst for VO^{2+}/VO_2^+ and chlorine evolution inhibitor in all-vanadium redox flow batteries

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1. Experimental

1.1. Materials

$VOSO_4$ (99.9%) was purchased from Alfa-Aeser. C_{76}, H_2SO_4, HCl, dimethylformamide (DMF) and polyvinylidene fluoride (PVDF) were purchased from Sigma-Aldrich. Carbon cloth was purchased from the Fuel Cell Store. All reagents were of analytical grade.

1.2. Preparation of electrodes

The thermal treatment of the as-received carbon cloth (untreated carbon cloth, UCC) was done at 450 ^{0}C for 10 h. 45 mg of C_{76} powder and 10 wt% PVDF binder were dissolved in ~ 3000 µl DMF and electromagnetically stirred overnight for homogeneity. Subsequent deposition of different C_{76} loadings (by brushing) on UCC and treated carbon cloth (TCC) electrodes (area ~ 1.7 cm^2), followed by oven-drying at 60 ^{0}C overnight took place.

1.3. Physiochemical characterization

The morphology of C_{76} was observed by field emission scanning electron microscopy (FESEM, Zeiss SEM Ultra 60, 5 kV) and high-resolution transmission electron microscope (HR-TEM, JOEL JEM-2100) operating at an accelerating voltage of 200 kV. Surface chemistry was studied by photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoScientific), Fourier transform infrared spectroscopy (FT-IR) *via* Perkin Elmer spectrometer using KBr FTIR grade, as well as Raman spectroscopy using a Raman microscope (ProRaman-LAnalyzer) with an excitation laser beam wavelength of 532 nm. The wettability of the electrodes was characterized by the water contact angle test using KRUSS DSA25.

1.4. Electrochemical characterization

A Biologic SP 300 workstation was employed for electrochemical measurements. Cyclic voltammetry (CV) was carried out in a three-electrode cell with the carbon cloth samples (UCC, TCC, UCC-C_{76}, and TCC-C_{76}) as the working electrode, saturated calomel electrode as the reference electrode and platinum coil as the counter electrode, at scan rates of 5, 10, 20 and 50 mV s^{-1}. All CV potential measurements were corrected to the SHE scale. IR correction was applied to avoid taking into account any ohmic losses. Electrochemical impedance spectroscopy (EIS) tests were performed over a frequency range of 0.01-10^5 Hz with a voltage perturbation of 10 mV at open circuit potential. The electrolyte used in the CV and EIS measurements was 0.1 M $VOSO_4$ in 1 M H_2SO_4 or 1 M H_2SO_4/ 1 M HCl (mixed acid). To investigate the activity retention of the electrodes, repetitive 100-cycle voltammograms were conducted at a scan rate of 5 mV s^{-1} for UCC and UCC-C_{76}.

2. Supporting results

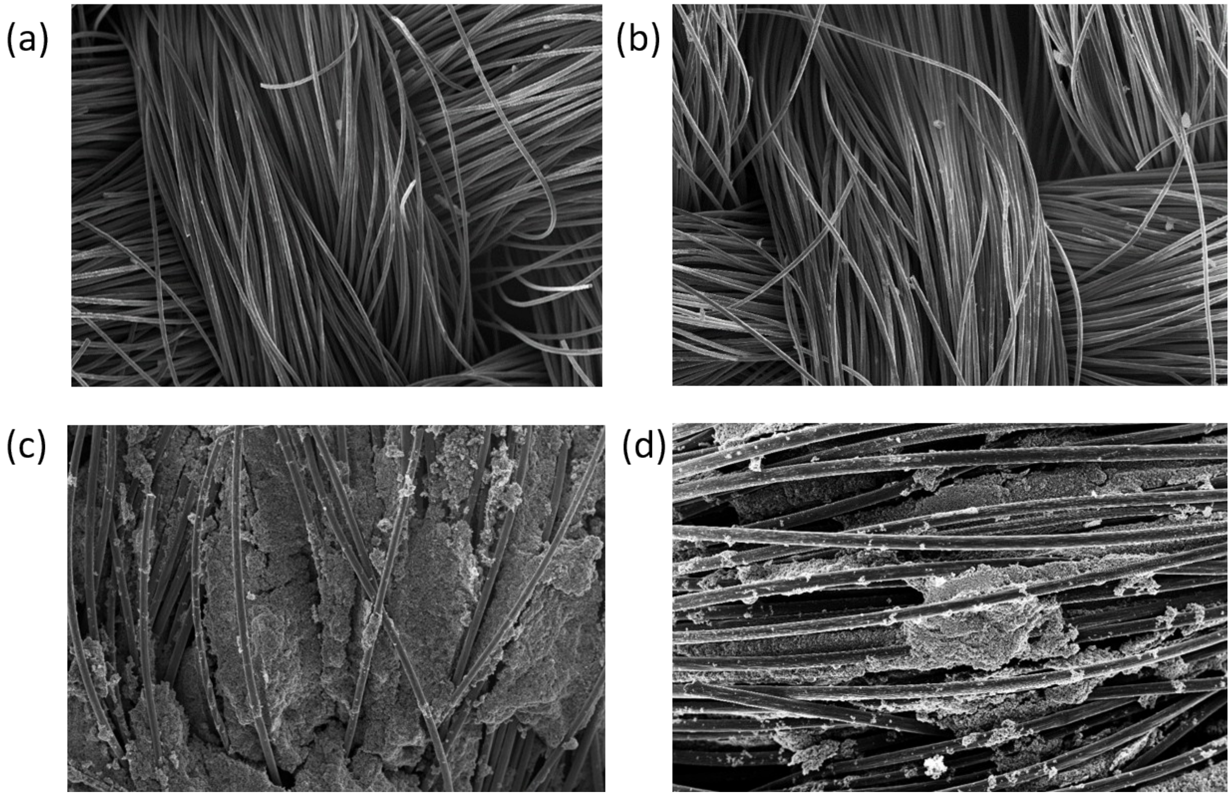

Fig. 1S shows the SEM images of (a) UCC, (b) TCC, (c) C_{76} on carbon cloth showing the penetration of C_{76} particles between the carbon cloth fibers and (d) close-up to show the distribution of C_{76} particles on carbon cloth

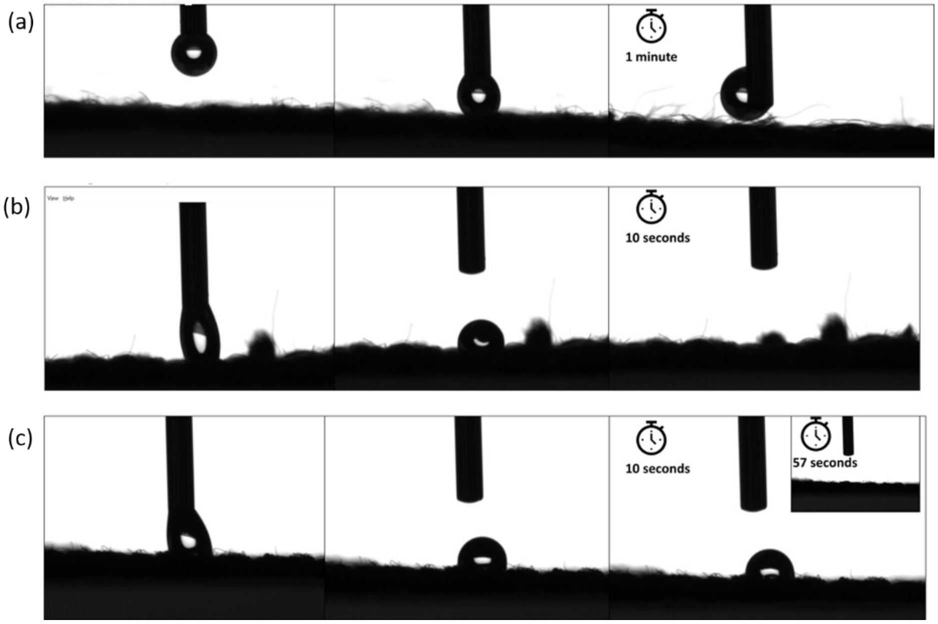

Fig. 2S shows the water contact angle measurements of (a) UCC, (b) TCC and (c) C_{76}. (a) Droplet would not attach to the surface showing very high hydrophobicity. (b) Droplet is immediately absorbed by the surface indicating excellent wettability of the electrode upon treatment. (c) Intermediate wettability, but the droplet gets completely absorbed within 57 seconds. In the presence of H_2SO_4, we believe that C_{76} might get oxidized in the first CV cycle due to and high oxidation potential.

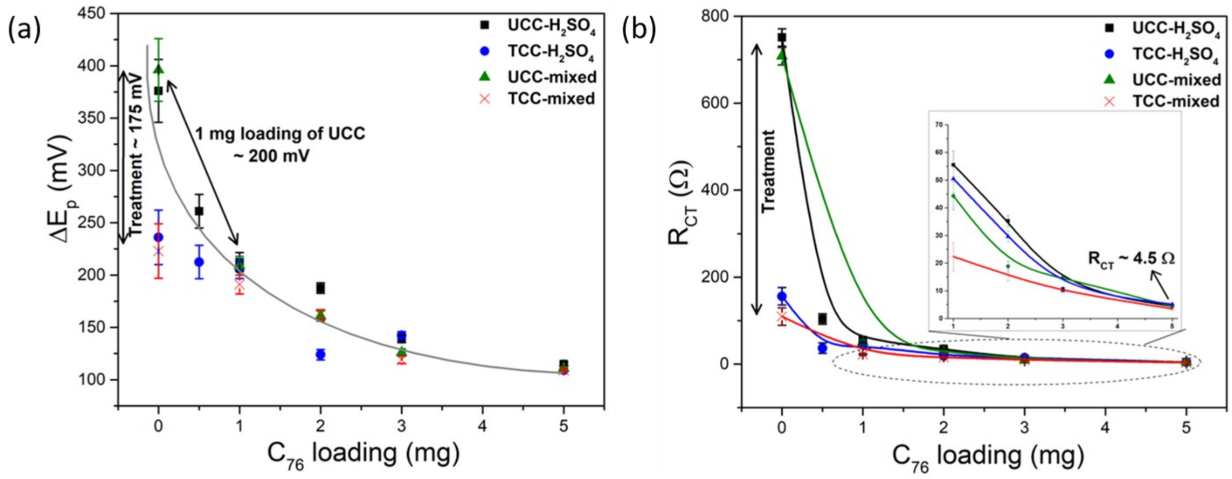

Fig. 3S shows the effect of different C_{76} loadings on the reversibility of the VO^{2+}/VO_2^+ electrochemical reaction in the 1st and 3rd generation of VRFBs. (a) Peak separation (obtained from CVs at a scan rate of 5 mV s^{-1}) decreases upon treatment (and no loading of C_{76}) by ~ 175 mV. With the addition of C_{76}, a value of ~ (109 ± 3) mV is reached at 5 mg loading. (b) Charge transfer resistance (obtained from EIS at open circuit potential) decreased from ~ (730 ± 20) Ω for UCC down to (4.5 ± 0.5) Ω for UCC-5 mg C_{76} and TCC-5 mg C_{76}.

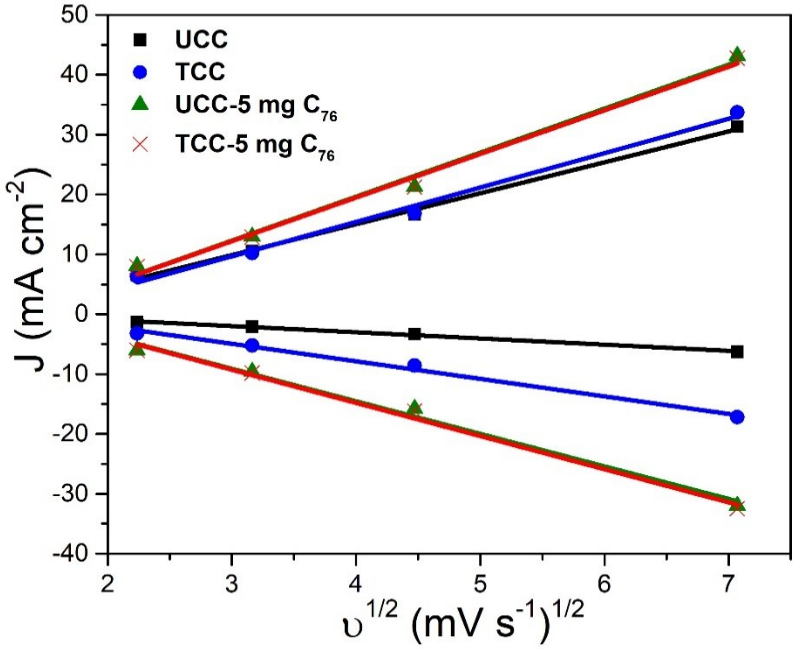

Fig. 4S shows the current density against the square root of the scan rate in the H_2SO_4 electrolyte. The linearity indicates no deviation from diffusion-controlled behavior due to the C_{76} loading, and vanadium ions could diffuse freely. Increasing the slope in the order C_{76} > TCC > UCC means not only better diffusion of vanadium ions from bulk to the electrode surface and *vice versa*, but also enhanced kinetics due to a higher number of active sites or mechanism change according to equation 1. The enhancement due to thermal treatment and incorporation of C_{76} is more significant in the case of the reduction reaction.

$$i_p = \left(2.99 \times 10^5\right) nAC(D\alpha)^{\frac{1}{2}} v^{\frac{1}{2}} \qquad (1)$$

Table 1S shows the Warburg slopes of UCC, TCC and C_{76} electrodes in both electrolytes. These are calculated from Nyquist plots in **Fig. 2b** and **Fig. 2d**. The Warburg slope increases in the order C_{76} > TCC > UCC, supporting the results of **Fig. 4S**.

Electrode	Electrolyte	
	H_2SO_4	Mixed acid
UCC	0.259	-
TCC	1.226	1.017
C_{76}	1.641	1.710