Nano letters

Supporting Information

Synergistic Effect of Carbon Nanofiber / Nanotube Composite Catalyst on Carbon Felt Electrode for High-performance All-Vanadium Redox Flow Battery

*Minjoon Park[1], Yang-jae Jung[1], Jungyun Kim[2], Ho il Lee[2], Jeaphil Cho[1]**

[1]School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 689-798, Ulsan, South Korea

[2]Energy Research Department, Industrial Research Institute, R & D Division, Hyundai Heavy Industries Co., Ltd., 446-912, Yongin, Gyeonggi, South Korea

***E-mail: jpcho@unist.ac.kr**

METHODS

Synthesis of CNF/CNT catalyst: A commercial carbon felt (PAN CF-20-3, Nippon carbon) was employed as electrode substrate. Prior to the surface modification, a carbon felt (CF) was washed by ultrasonication for 20 min in acetone and dried for 4 h at 100 °C in oven. The CF immersed in nickel nitrate solution (1 wt% Ni $(NO_3)_2$)(97%, Junsei, Japan) dissolved in acetone (60 mL)) was dried for 3 h at 100 °C. The deposited catalysts were calcined in an inert atmosphere and subsequently reduced in a mixture of hydrogen and 10 % H_2/balance Ar gas at 600 °C for 3 h, and cooled down to room temperature. To grow CNF/CNT catalyst, each samples were placed in a tube furnace under inert gas flow (0.5 L/min), heated to 500, 600, 700, and 800 °C (5 °C/min), respectively. After turning off the Ar flow, a flow of acetylene (9.94 % C_2H_2/balance Ar gas) was supplied to initiate CNF/CNT growth for 10 min, then cooled down to room temperatures under an inert gas. As-grown CNF/CNT-T was refluxed in concentrated hydrochloric acid for 2 h to introduce surface oxygen groups and to remove metal impurities. After extended washing in distilled water, the samples were dried at 100 °C in air for 12 h.

Characterization: The material morphology was examined by FE-SEM (S-4800, Hitachi) operating at 10 kV and HR-TEM (JEM2100, JEOL) operated at 200 kV. XRD pattern was obtained on an X-ray diffractometer (D/Max2000, Rigaku). Surface elemental composition was analyzed with XPS (Thermo Fisher, UK). A potentionstat/galvanostat (WonAtech) was used to evaluate the electrochemical properties. BET measurement was used to determine the specific surface area of electrodes (ASAP2420, Micromeritics). Electrochemical impedance spectrum (EIS) was measured on single potentiostat (Ivium) by applying an alternating voltage of 5 mV over the frequency ranging from 10^{-2} to 10^5 Hz.

Electrochemical test: The cyclic voltammograms (CV) were obtained using a three

electrode cell. The carbon felt working electrode with the diameter of 6 mm was connected to platinum wire with a reference electrode (Ag/AgCl), and counter electrode (Pt mesh) in 0.1 M $VOSO_4$ (Aldrich, 99.5%) in 3 M H_2SO_4 solution (Aldrich, 98%) at different scan rate range from 1 to 10 mV/s. A VRFB single flow cell was assembled for electrochemical test. Electrolytes were prepared by dissolving 2 M $VOSO_4$ in 3 M H_2SO_4 solution. The untreated and as-prepared electrode with an active area of 5 cm^2 was used as positive and negative electrode, respectively. Nafion113 ion exchange membrane was employed and graphite plate was placed between electrode and copper current collectors. The test cell was charged and discharged from 1.6 to 0.8 V with a current density of 40 $mA \cdot cm^{-2}$ to 100 $mA \cdot cm^{-2}$.

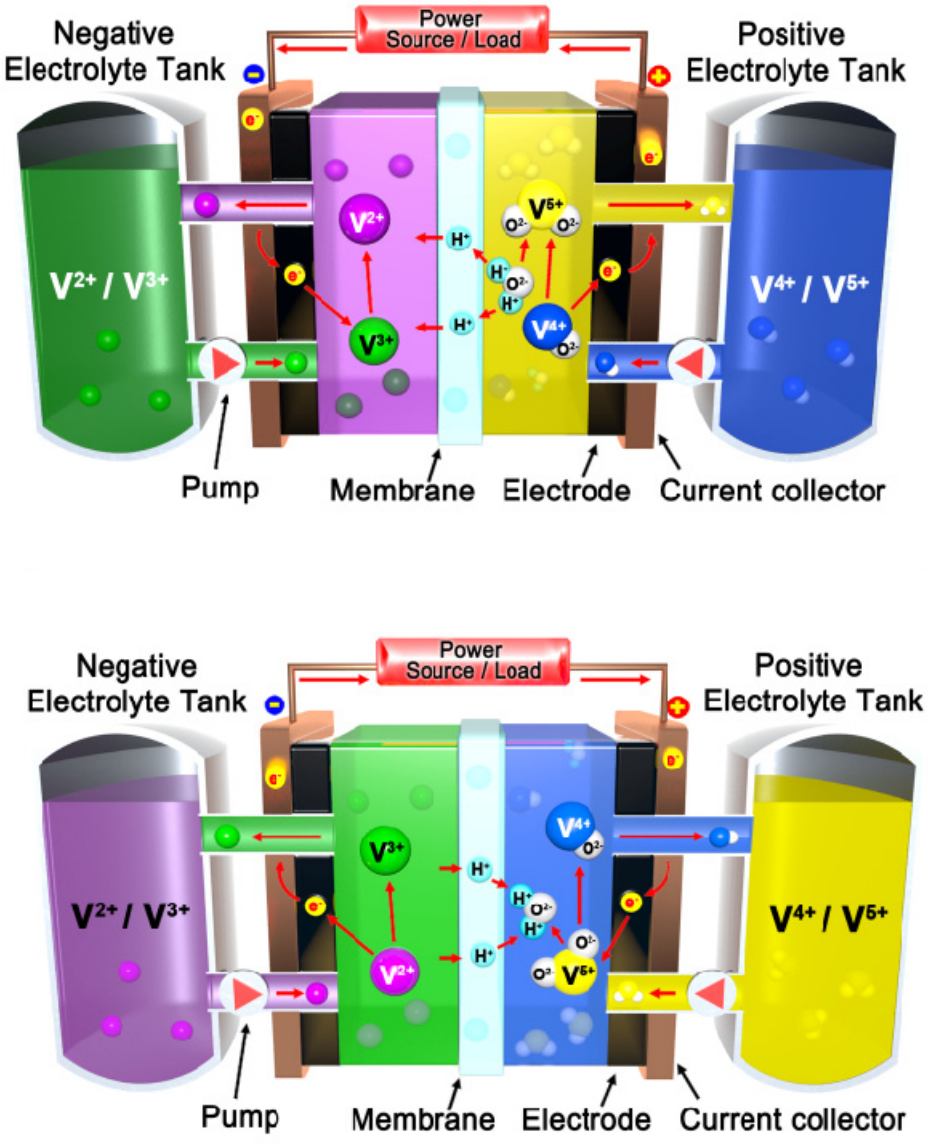

Figure S1. A schematic illustration of a vanadium redox flow battery comprised of two main electrolyte tank, electrode compartment separated by membrane separator. (upper: charging, lower: discharging)

Table S1. Summary of electrochemical properties of various 1D carbon nanomaterials as electrode material/catalysts to improve battery performance and electrochemical activity in sulfuric acid-based electrolyte for VRFB system (CF: carbon felt, GF: graphite felt, GO: graphene oxide)

Cell type	Modification method	Based material	Catalyst	Full-cell		Half-cell	Ref.
				Current density (mA/cm^2)	CE / VE / EE (%)	ΔE (mV)	
Flow cell	**C_2H_2 decomposition**	**CF**	**CNF/CNT**	**40 (100)**	**96.8 / 87.5 / 85 (97.2 / 67.5 / 65.6)**	**136**	**This work**
Flow cell	Solution immersion	CF	MWCNT	20 (80)	- / - / 86.5 (- / - / 66.7)	-	[22]
Flow cell	Solution immersion	CF	MWCNT	50	93.9 / 87.3 / 82.0	252	[29]
Flow cell	CVD	GF	N-CNT	10	81.33 / 94.7 / 77.0	-	[30]
Static cell	Solution immersion	CF	SWCNT	20	93 / 90 / 83.7	190	[24]
Static cell	Solution immersion	CF	MWCNT	20 (70)	97.5 / 91.2 / 88.9 (98.6 / 76.1 / 75.0)	111	[26]
Half-ell	Composite	GO	MWCNT	-	- / - / -	150	[11]

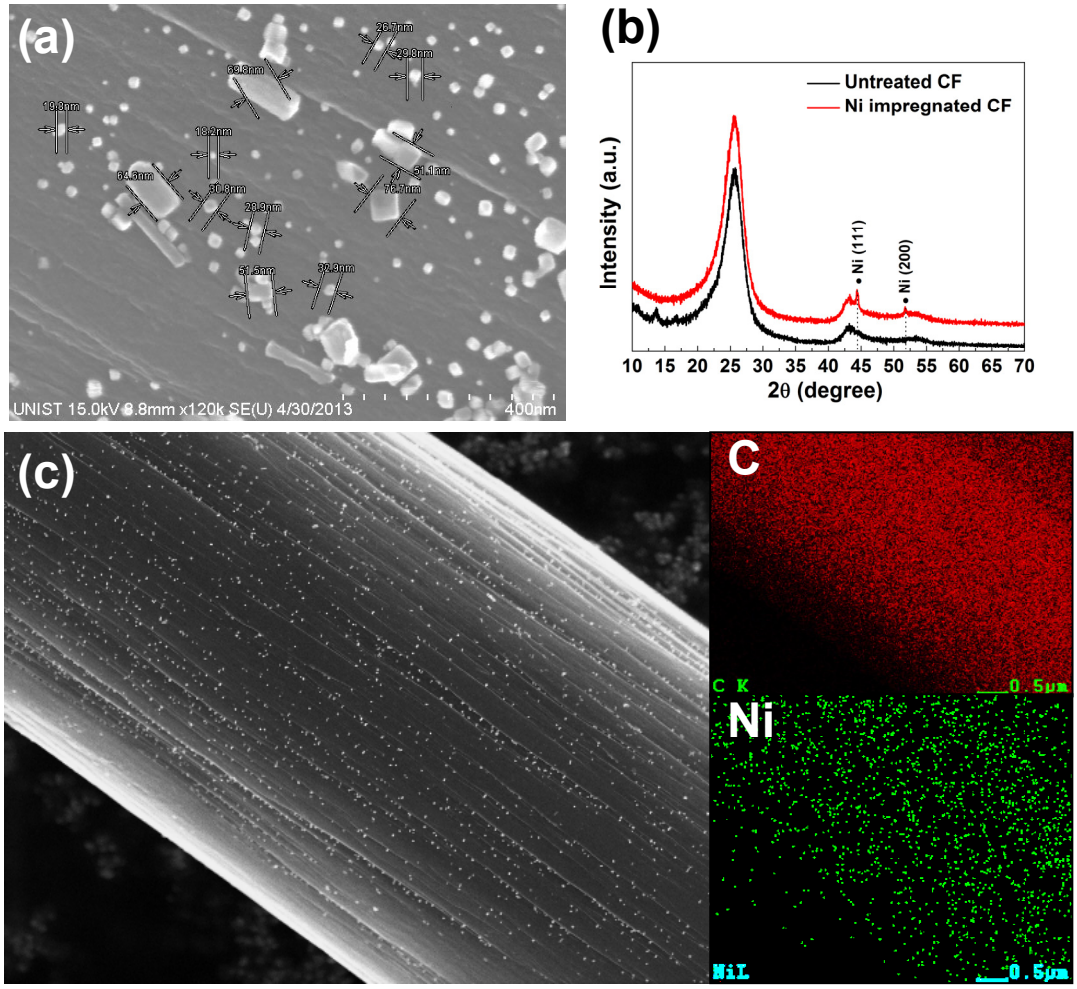

Figure S2. (a) SEM image of Ni nanoparticle formed on CF, (b) XRD patterns of the untreated and as-prepared nickel impregnated CF electrode, and (c) The SEM image of as-prepared nickel impregnated CF electrode and its EDXS mapping of carbon and nickel element.

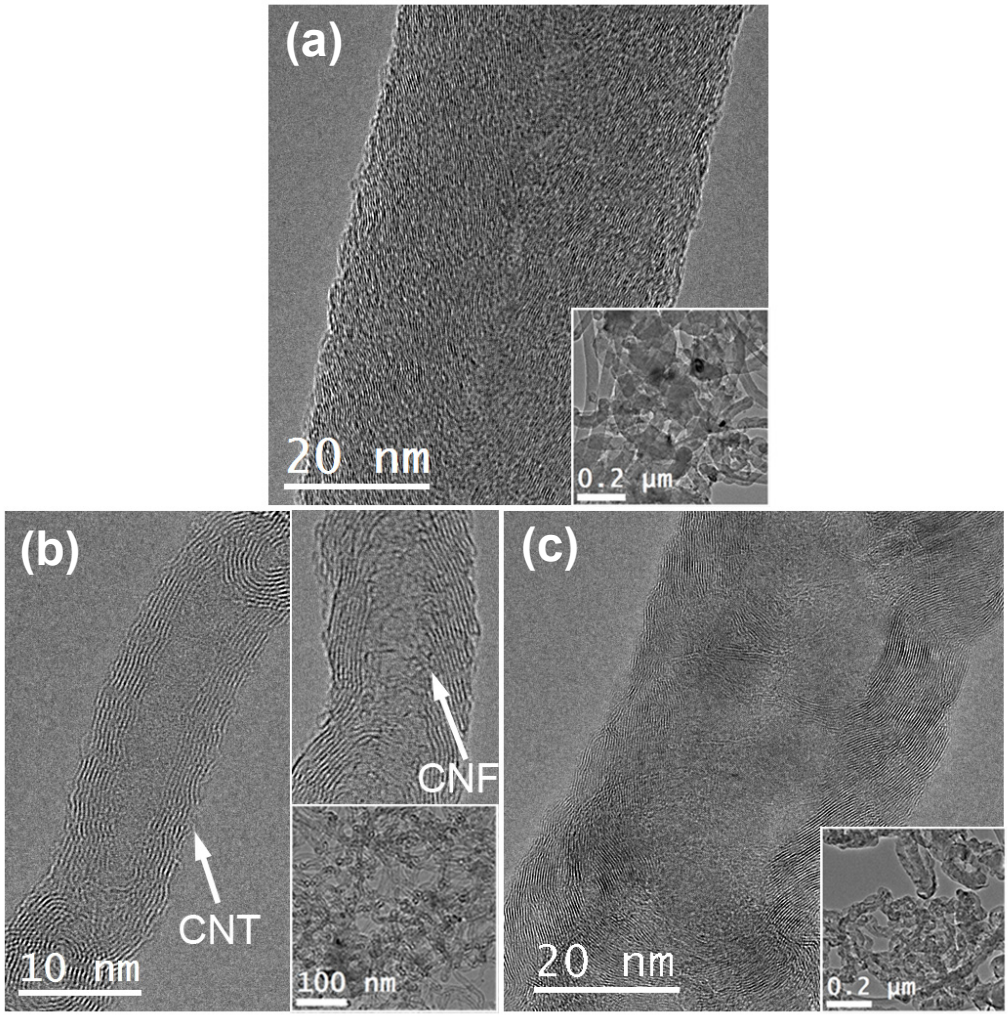

Figure S3. HR-TEM images of the detached samples from the carbon felt after C_2H_2 treatment at (a) 500 °C, (b) 600 °C, and (c) 800 °C

Under annealing at 500 °C, most of carbon nanofibers consist of turbostratic graphene plane with no crystalline structure (**Figure S3a**). When temperature was increased to 600 °C, mixed CNF and CNT are formed, which is similar to the CNF/CNT-700 sample. At 800 °C (see **Figure S3c**), mixed CNF and CNT phase seem to be disappeared and collapsed CNF with crystalized graphitic wall was mainly observed. It should be noted that the sample prepared at 800 °C showed the destruction of CNF/CNT structure.

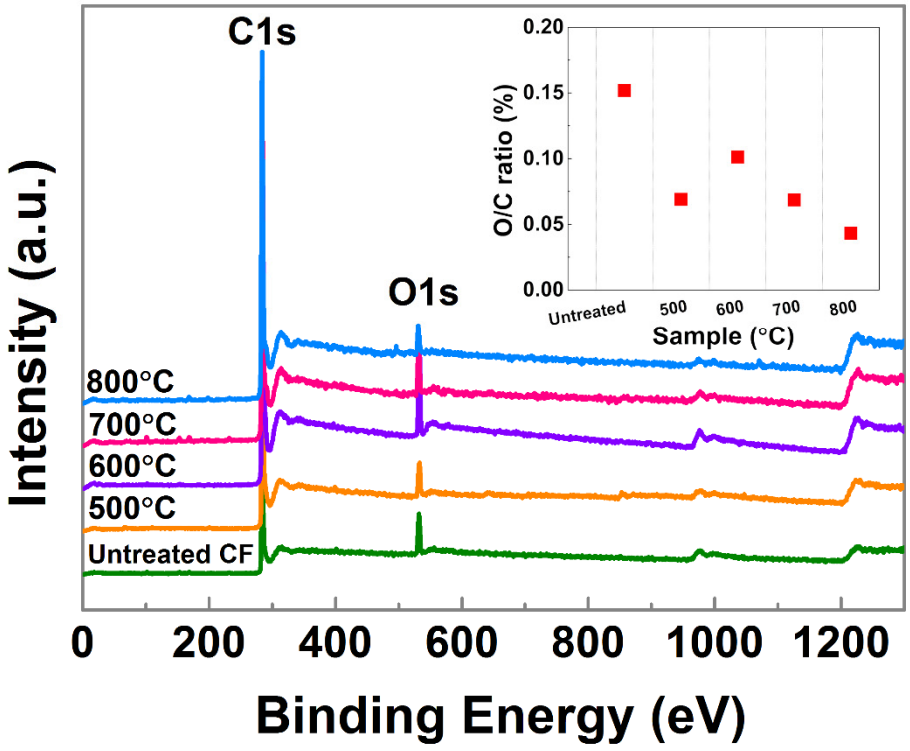

Figure S4. Ex-situ X-ray photoelectron spectroscopy analysis of the CNF/CNT-T samples. XPS survey with inset image of the ratio of O/C contents.

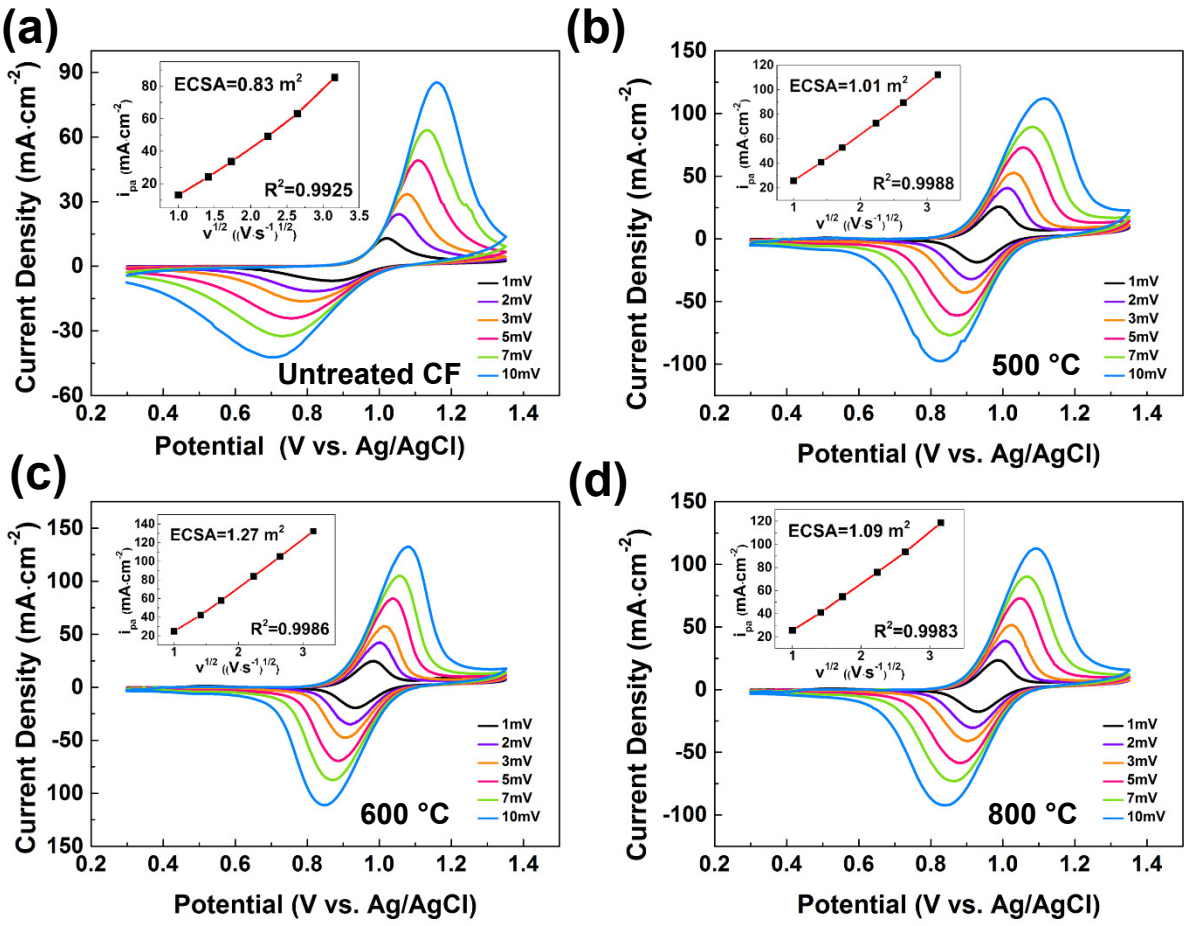

Figure S5. Cyclic voltammetry curves on the untreated CF and CNF/CNT-T electrode in 0.1 M $VOSO_4$ + 2 M H_2SO_4 electrolyte solution at different scan rate. (a) untreated CF, (b) T=500 °C, (c) T=600 °C, and (d) T=800 °C. Inset: plot of the anodic peak current (i_{pa}) versus the square root of the potential scan rate.

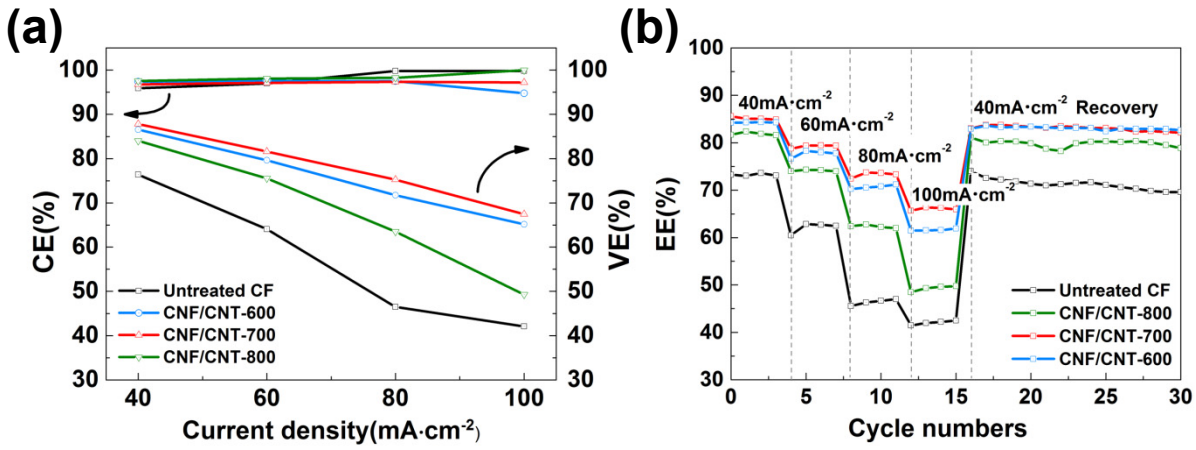

Figure S6. (a) CE and VE, and (b) EE value as a function of cycle number at different current rate.

The coulomb efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) values under current density range from 40 to 100 mA·cm^{-2} are plotted in **Figure S6a and b**. The CE, the ratio of between charge and discharge capacity of VRFB, showed no significant difference, while the VE, the ratio of charge and discharge voltage, exhibited considerable difference as increasing the current density. The VE value on CNF/CNT-700 electrode was 10.9 % higher compared to that on untreated CF at 40 mA·cm^{-2}. Furthermore, at a current rate of 100 mA·cm^{-2}, the high voltage efficiency of 67.5 % on CNF/CNT-700 sample compared with that on 42.1 % at untreated one was achieved. **Figure S6b** also shows the EE, obtained by CE and VE values (EE = CE × VE), was highest on CNF/CNT-700 electrode, which was in the order 85, 79, 73 and 66 % at a rate of 40, 60, 80 and 100 mA·cm^{-2}, respectively, compared to that on untreated one in the order 73, 61, 46 and 41 % at the same current rate. Such enhanced properties could probably be attributed to the increased conductivity by growing CNT and outer-oriented edge planes of graphene walls of CNF.

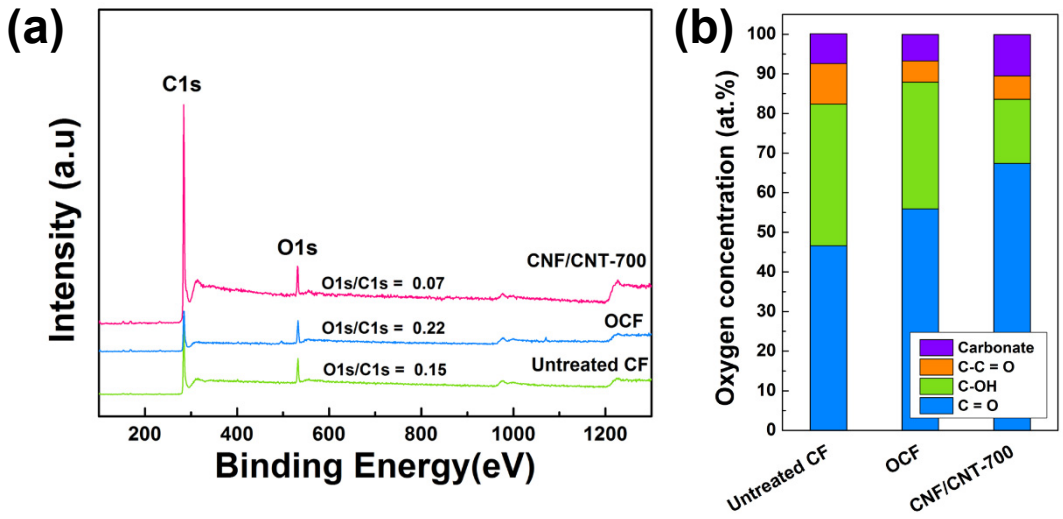

Figure S7. (a) Ex-situ X-ray photoelectron spectroscopy(XPS) analysis of the untreated, oxidized, and CNF/CNT-700 CF, and (b) Chemical composition ratio of functional groups from curve fitting of O1s XPS spectra of OCF sample.

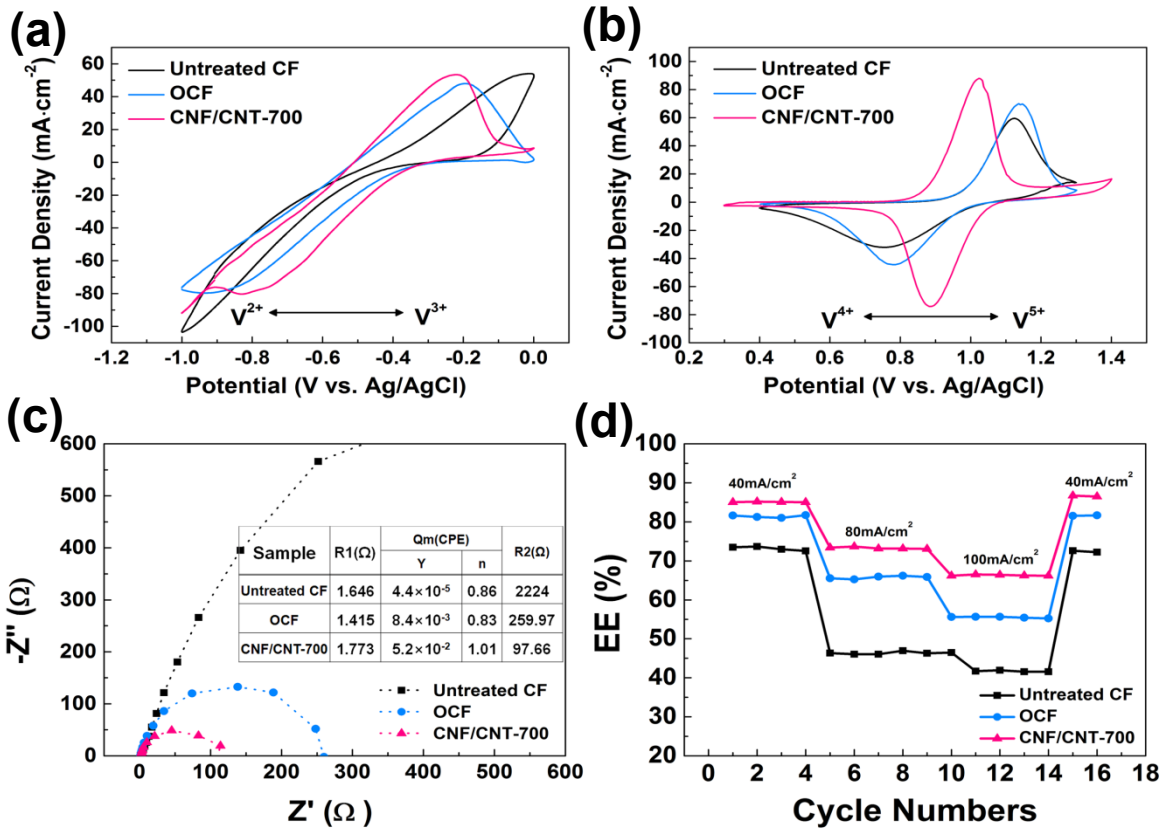

Figure S8. Cyclic voltammograms with the untreated, oxidized, and CNF/CNT-700 CF as working electrode (a) for V^{2+}/V^{3+} redox couple in negative electrolyte, and (b) for VO^{2+}/VO_2^{+} redox couples in positive electrolyte at the scan rate of 5mV s^{-1}, respectively. (c) Nyquist plot showing electrochemical impedance spectroscopy (EIS) data for the untreated, oxidized, and CNF/CNT-700 CF in 0.1 M $VOSO_4$ + 2 M H_2SO_4 electrolyte solution. (d) Energy efficiency (EE) value as a function of cycle number at different current rate.

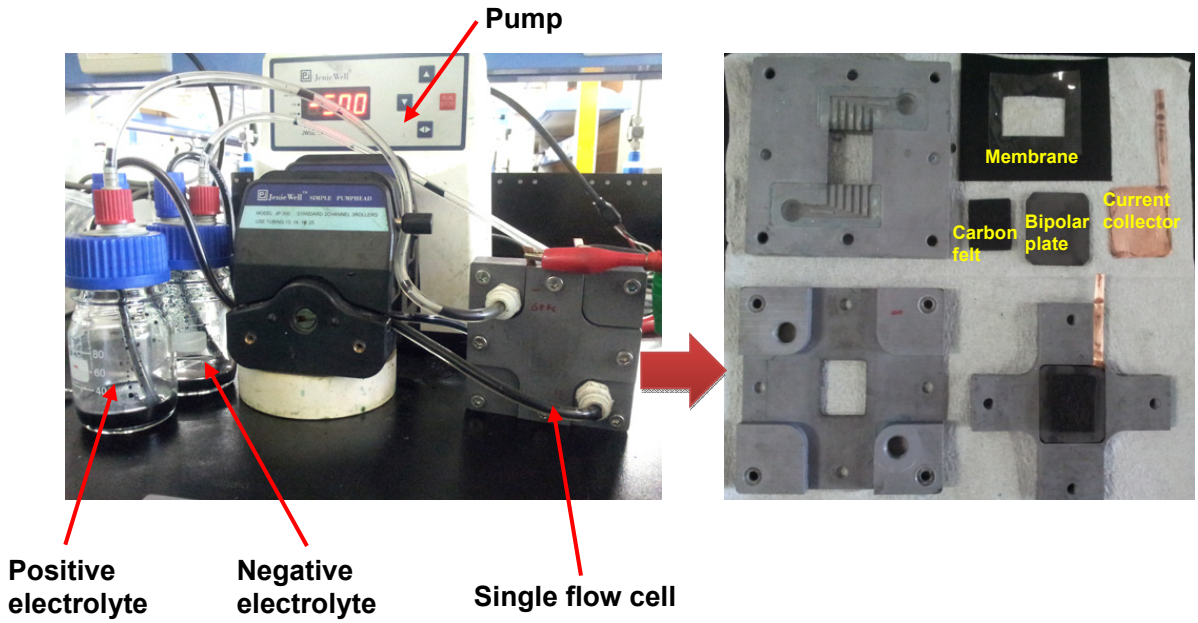

Figure S9. Vanadium redox flow battery system, which includes a single stack cell (composed of the electrode, membrane, bipolar plate, and current collector), two electrolyte tank, and flow pump.