Electronic Supplementary Information (ESI)

Excellent Electrocatalytic Effect of Tin through *in-situ* Electrodeposition on the Performance of All-Vanadium Redox Flow Batteries

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In VRFB, electrolyte circulates through the cell where the redox reactions take place under galvanostatic conditions of charge / discharge. Catholyte consists of 1.5 M VO^{2+} / 3.0 M H_2SO_4 where as anolyte is 1.5 M V^{3+} / 3.0 M H_2SO_4, with a total sulfate concentration of 4.5 M. During charging, VO^{2+} is converted to VO_2^+ in the catholyte with the corresponding change in color from blue to yellow where as V^{3+} gets converted to V^{2+} with the corresponding change in color from green to purple. This unique specialty with the four vanadium species give this system the name of "all-vanadium", thus minimizing the cross contamination of redox couples rendering it a longer life. The opposite reactions take place during discharge conditions. The electrochemical equations governing these redox reactions during charging are;

Cathode: $VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$ $E^o = 1.00$ V vs. SHE (S1)

Anode: $V^{3+} + e^{-} \rightarrow V^{2+}$ $E^{o} = -0.25$ vs. SHE (S2)

In monitoring of VRFB performance, the experimental conditions (electrolyte concentration, electrolyte volume, electrolyte flow rate, electrolyte material and size, membrane, voltage window, current density) and parameters of CE, VE, EE, specific discharge capacity, specific discharge energy density, capacity retention, and electrolyte utilization from the galvanostatic charge / discharge measurements are important.

Theoretical capacity of the electrolyte is calculated using the relation

Specific theoretical capacity (Ah L^{-1}) =

(Concentration of electrolyte (M) × Faraday Constant (C mol^{-1}) ×Number of electrons) / 3600

Capacity retention at a specific current density is calculated by

Capacity retention = (Capacity at the i^{th} cycle / Capacity at the 2^{nd} cycle)

The experimental conditions are;

Electrode: Carbon felt (TOYOBO XF 30A) with active area 25 cm^2

Membrane: Nafion 117

Electrolyte Concentration: 1.5 M

Electrolyte Volume: 50 mL of each anolyte and catholyte

Electrolyte Flow Rate: 50 mL min^{-1}

Current density: 50 -150 mA cm^{-2}

Voltage Window: 1.60 - 0.7 V

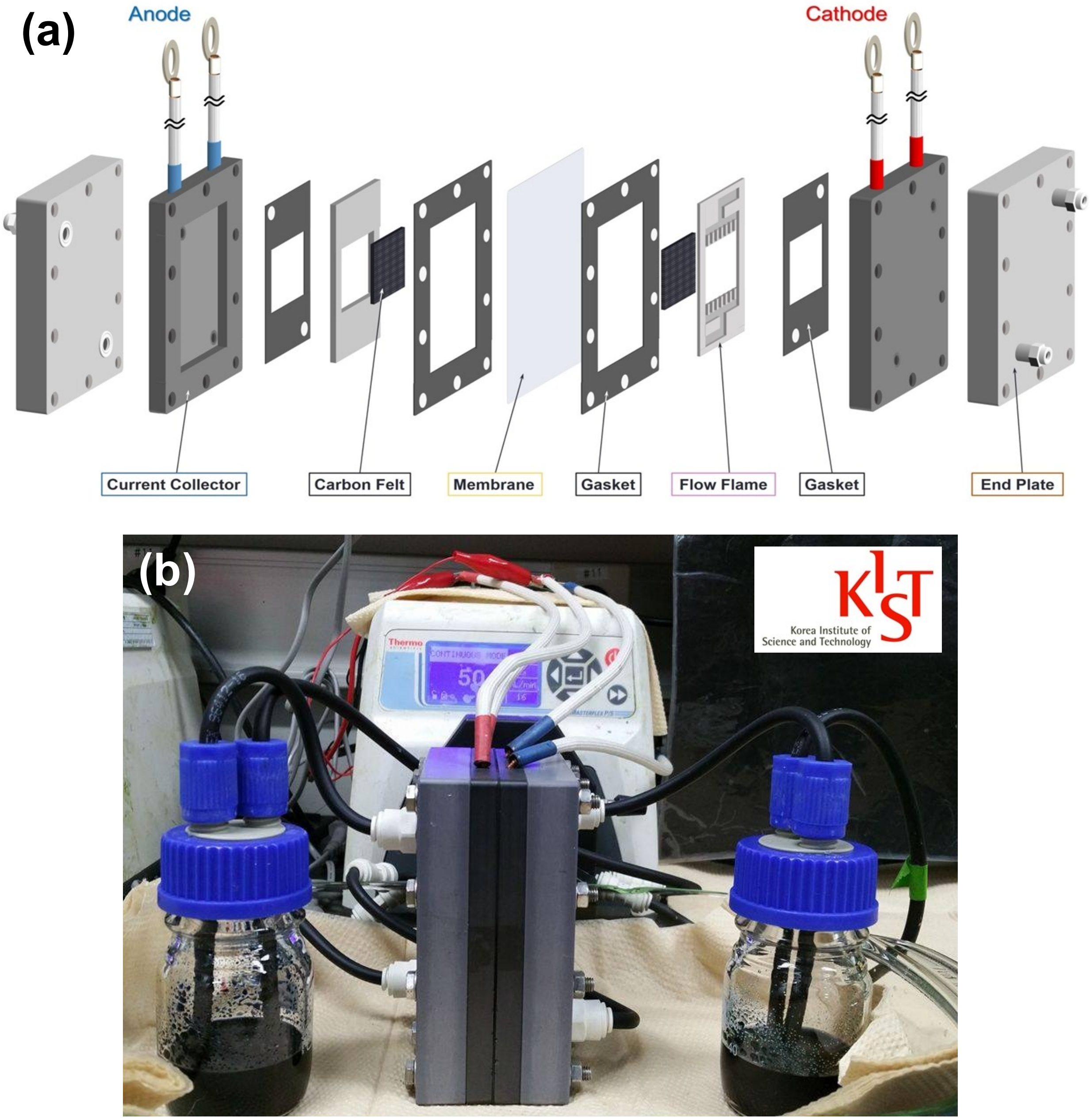

Fig. S1 (a) Schematic of the cell fixture used for VRFB performance and (b) VRFB set up.

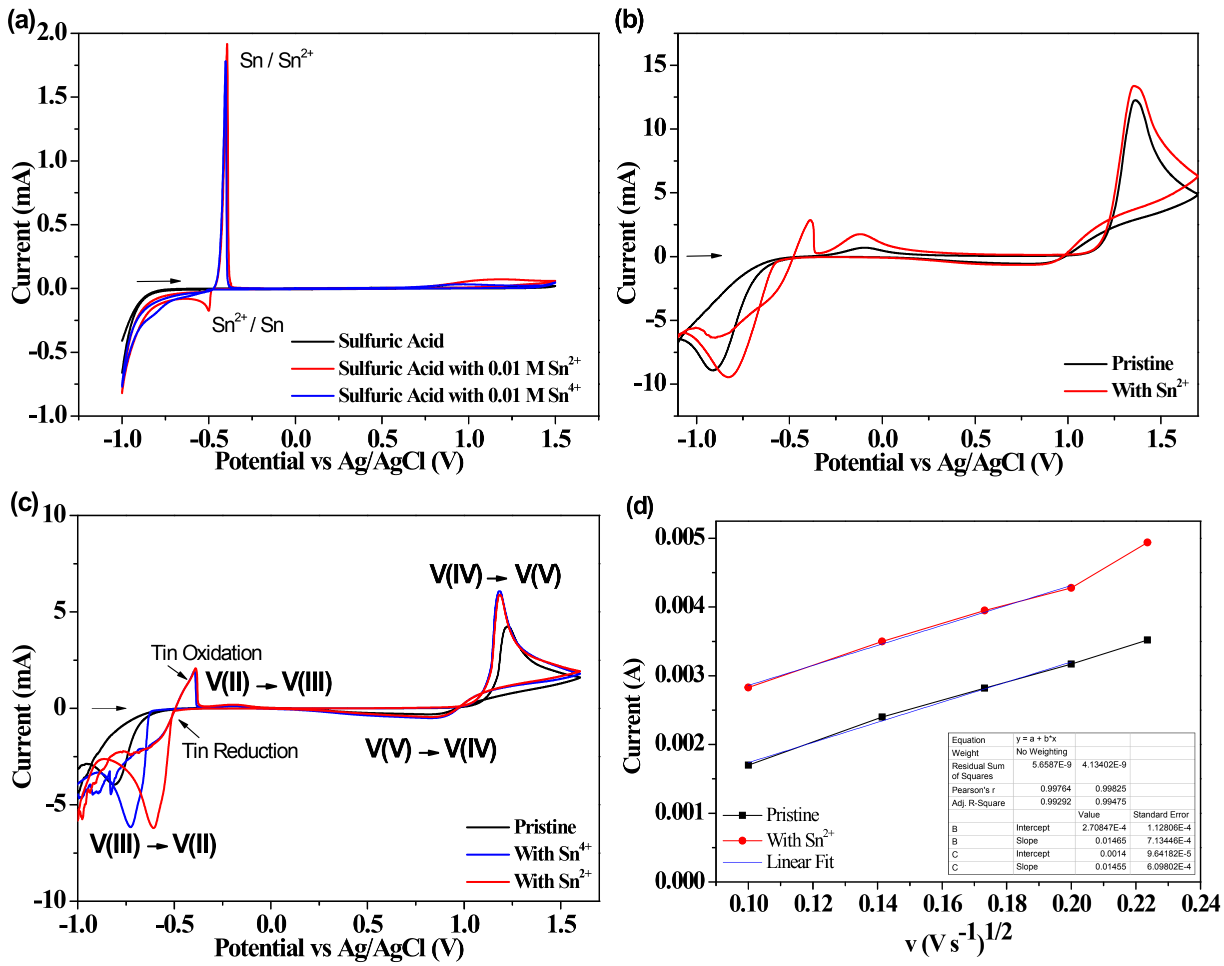

Fig. S2 (a) CVs of 3 M sulfuric acid with 0.01 M of Sn^{2+} or Sn^{4+} ions at scan rate of 50 mV s^{-1}; (b) CVs of 1.5 M V^{3+} / 3 M H_2SO_4 with 0.01 M of Sn^{2+} at scan rate of 50 mV s^{-1} ; (c) CVs of 1.5 M VO^{2+} / V^{3+} (1:1) in 3 M H_2SO_4 with 0.01 M of Sn^{2+} or Sn^{4+} at scan rate of 10 mV s^{-1} and (d) Current vs. square root of scan rate for V^{3+} / V^{2+} reduction reaction.

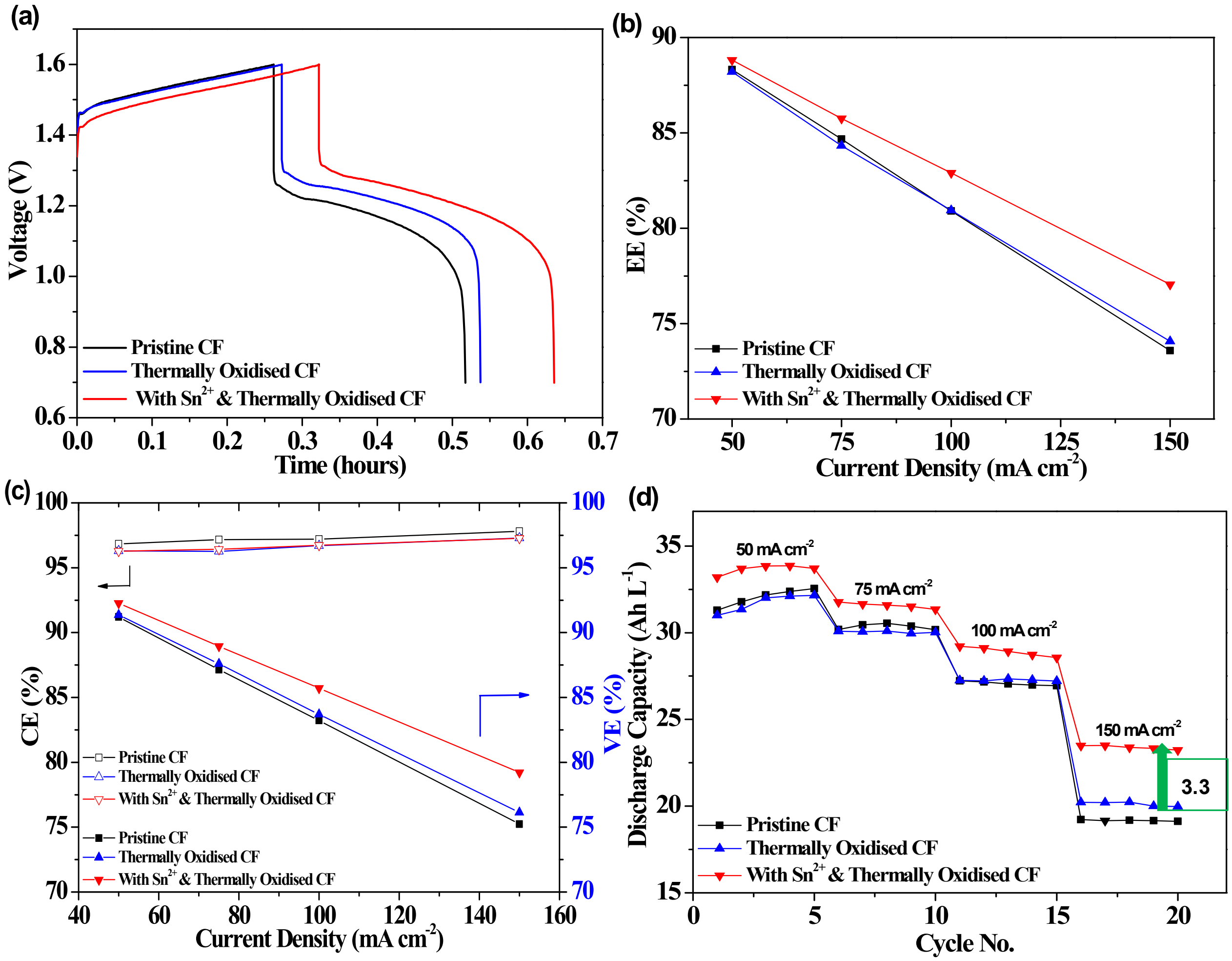

Fig. S3 VRFB performance with thermally oxidized carbon felt and 0.01 M Sn^{2+} in both anolyte and catholyte (a) galvanostatic charge / discharge at 150 mA cm^{-2}; (b) EE at various current densities; (c) CE and VE at various current densities and (d) Specific discharge capacity with pristine and thermally treated CF with / without 0.01 M Sn^{2+}.

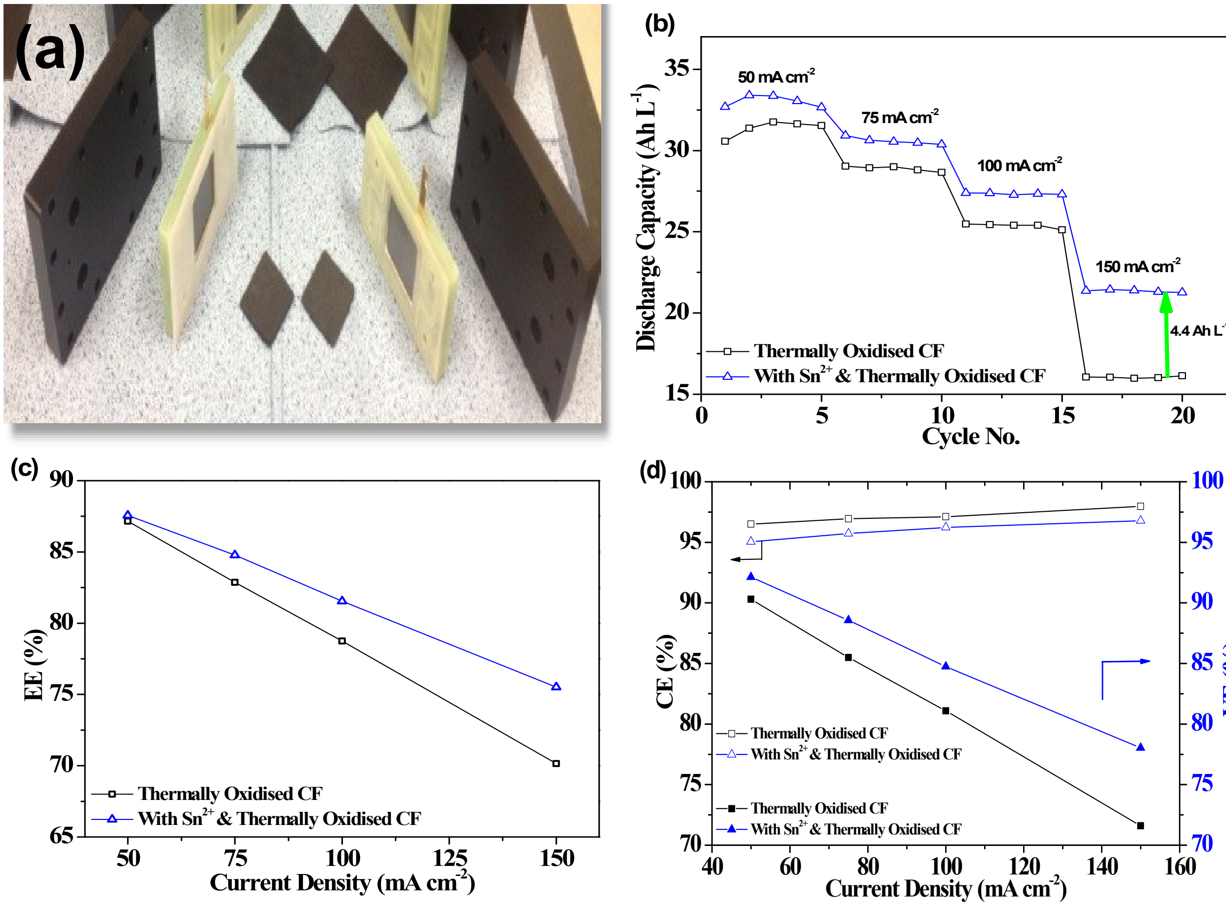

Fig. S4 VRFB performance in a different cell fixture with thermally oxidized CF and 0.01 M of Sn^{2+} ions in both anolyte and catholyte (a) Photograph of a different cell fixture; (b) Specific discharge capacity at various current densities; (c) EE at various current densities and (d) CE and VE at various current densities.

(For VRFB performance with cell fixture of Fig. S4a, same cell components and testing conditions were used as those for Fig. S3, except the cell design.)

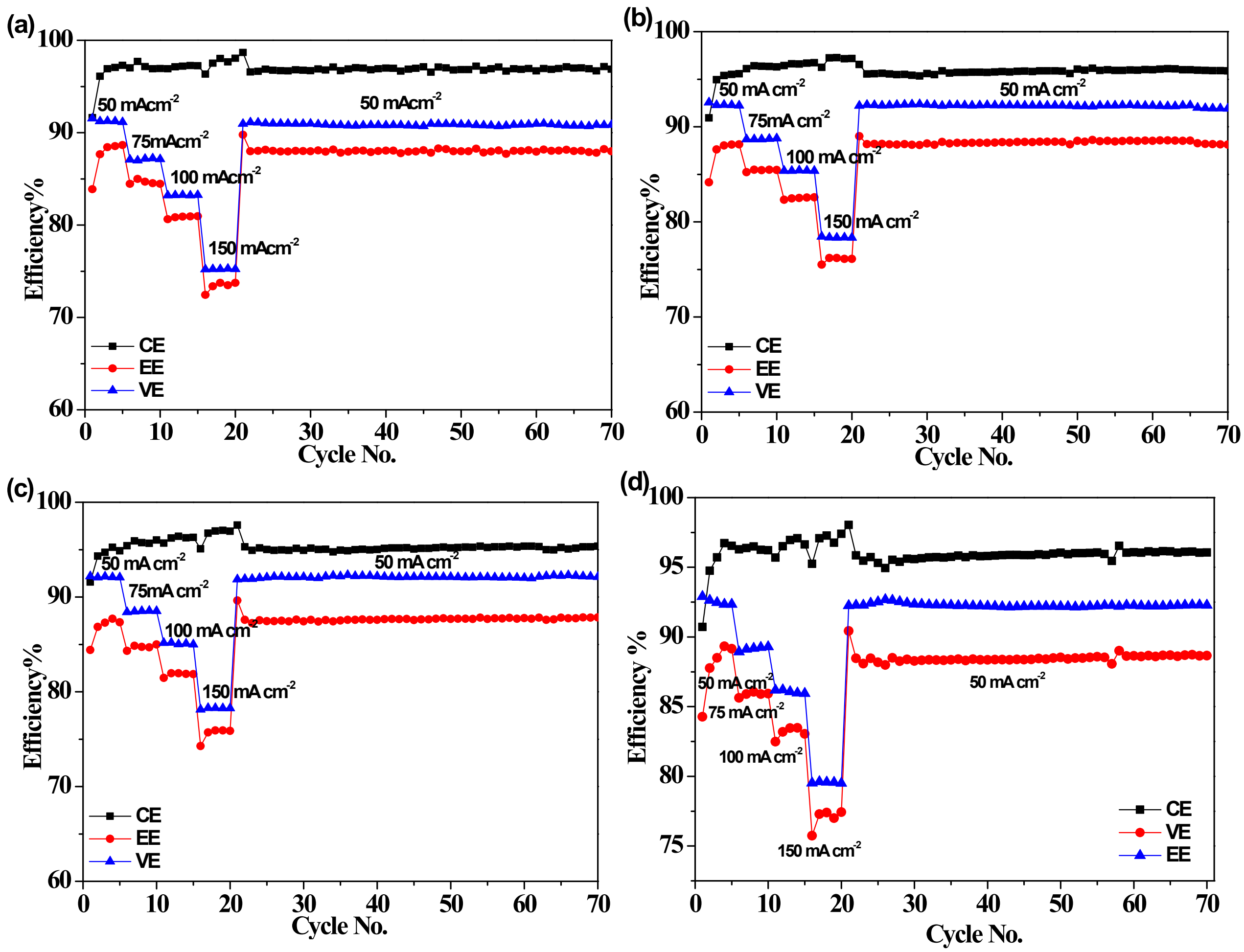

Fig. S5 VRFB Cycling in terms of CE, VE and EE (a) pristine; (b) with 0.01 M Sn^{2+} in both anolyte and catholyte; (c) with 0.01 M Sn^{2+} in catholyte only and (d) with 0.01 M Sn^{2+} in anolyte only.

Table S1. Performance comparison with few recently reported electrocatalysts for VRFB.

Sr. No	Catalyst		Without Catalyst		With Catalyst		Reference
		Current density (mA cm^{-2})	Specific Disc. Cap. (Ah L^{-1})	EE (%)	Specific Disc. Cap. (Ah L^{-1})	EE (%)	
1.	**Tin**	**150** **100** **50**	**19.2** **27.0** **32.2**	**73.6** **80.9** **88.3**	**24.2** **29.8** **33.3**	**77.3** **83.5** **89.3**	**This Work**
2.	Phosphate-doped CF	120	-	60	-	75	*Chemsuschem.,* 2016, **9**, 1329.
3.	Edge-halogentated Graphene nanoplatelet	50	9	66	17	86.8	*Nano Energy,* 2016, **26**, 233.
4.	Graphene Nanowall	125	-	-	-	73	*Adv. Sci.,* 2015, 1500276.
5.	N-Doped GF	150	5.2	61.6	16.2	74.2	*J. Mater. Chem. A,* 2015, **3**, 12276.
6.	N-doped Carbon	150	0	25	10	68.8	*Energy Environ. Sci.,* 2014, **7**, 3727.
7.	Niobium Oxide	150	8	66	14	77	*Nano Lett.,* 2014, **14**, 158.
8.	Graphene nanoplatelet	150	-	25	-	70	*Adv. Energy Mater.,* 2014, 1401550.
9.	Bismuth	150	8.04	66	17.2	77	*Nano Lett.,* 2013, **13**, 1330.
10.	Carbon Nanofiber / nanotube	100	0	41	8	65.6	*Nano Lett.,* 2013, **13**, 4833.

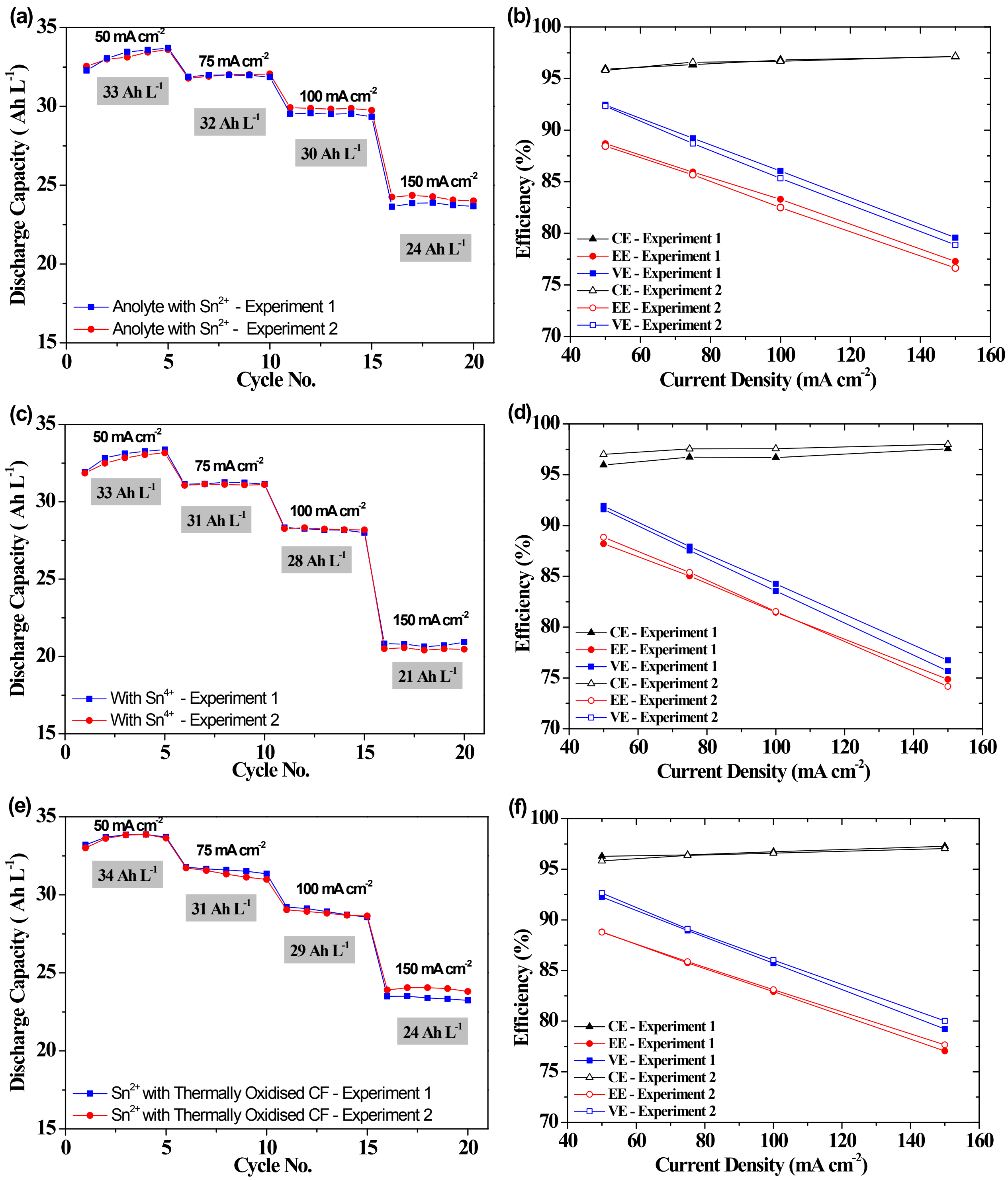

Fig. S6 Reproducibility tests for VRFB performance (a and b) anolyte with 0.01 M of Sn^{2+}; (c and d) with 0.01 M Sn^{4+} in both anolyte and catholyte; (e and f) with 0.01 M of Sn^{2+} in both anolyte and catholyte.

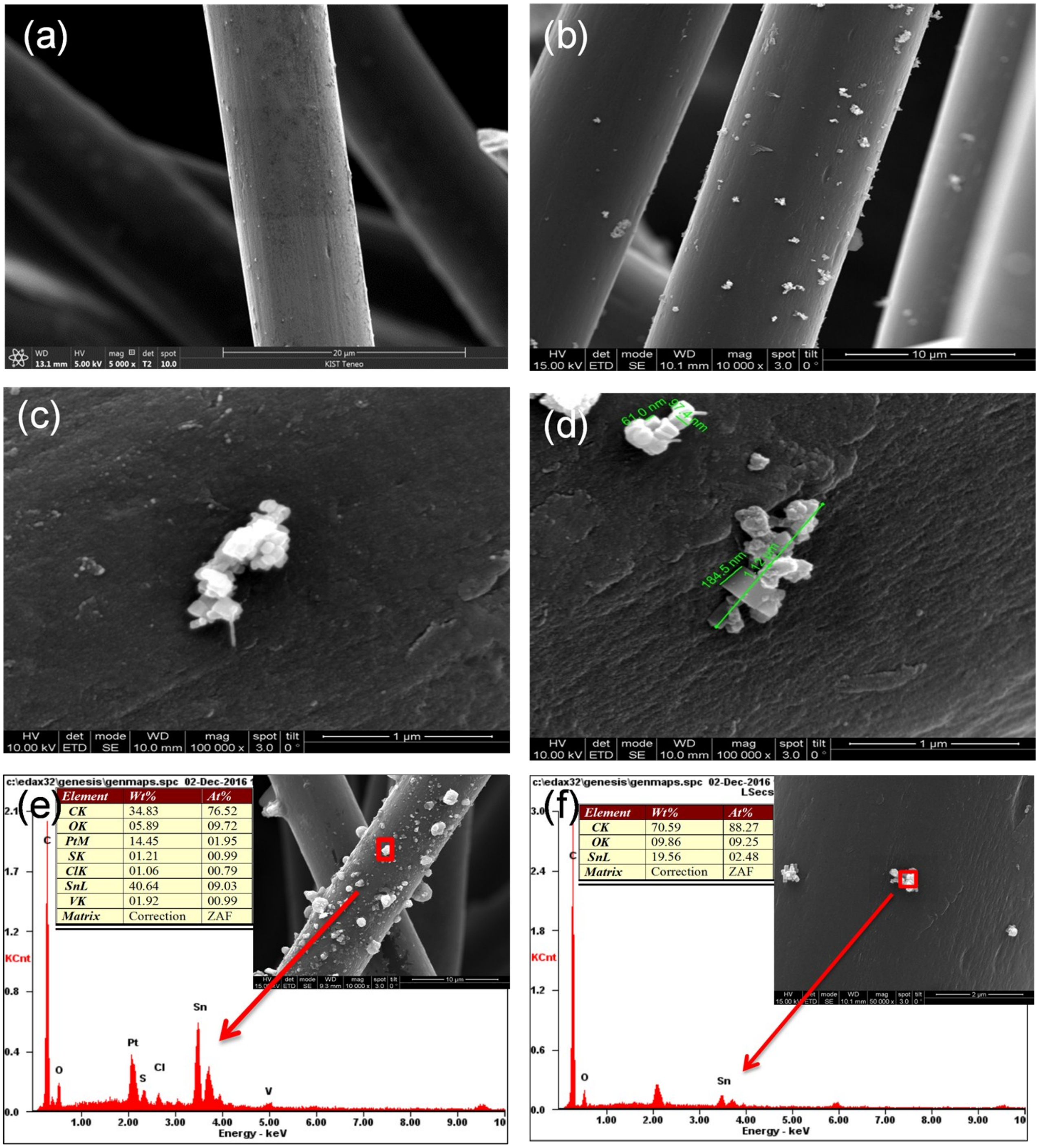

Fig. S7 SEM images (a) anode side of pristine cycled CF; (b,c and d) anode side of CF cycled with 0.01 M Sn^{2+} in both anolyte and catholyte at different magnifications; (e) SEM-EDS of the cathode side of CF cycled with Sn^{2+} in both anolyte and catholyte and (f) SEM-EDS of anode side of (e).

Table S2. Conductivity of electrolyte samples.

Sr. No.	Electrolyte Sample	Conductivity [mS cm^{-1}]
1.	1.5 M V^{4+} / 3 M H_2SO_4	374
2.	1.5 M V^{4+} / 3 M H_2SO_4 with 0.01 M Sn^{2+}	370
3.	1.5 M V^{3+} / 3 M H_2SO_4	289
4.	1.5 M V^{3+} / 3 M H_2SO_4 with 0.01 M Sn^{2+}	306
5.	1:1 of 1.5M V^{4+} : V^{3+} / 3 M H_2SO_4	329
6.	1:1 of 1.5 M V^{4+} : V^{3+} / 3 M H_2SO_4 with 0.01 M Sn^{2+}	325
7.	1:1 of 1.5 M V^{4+} : V^{3+} / 3 M H_2SO_4 with 0.01 M Sn^{4+}	326

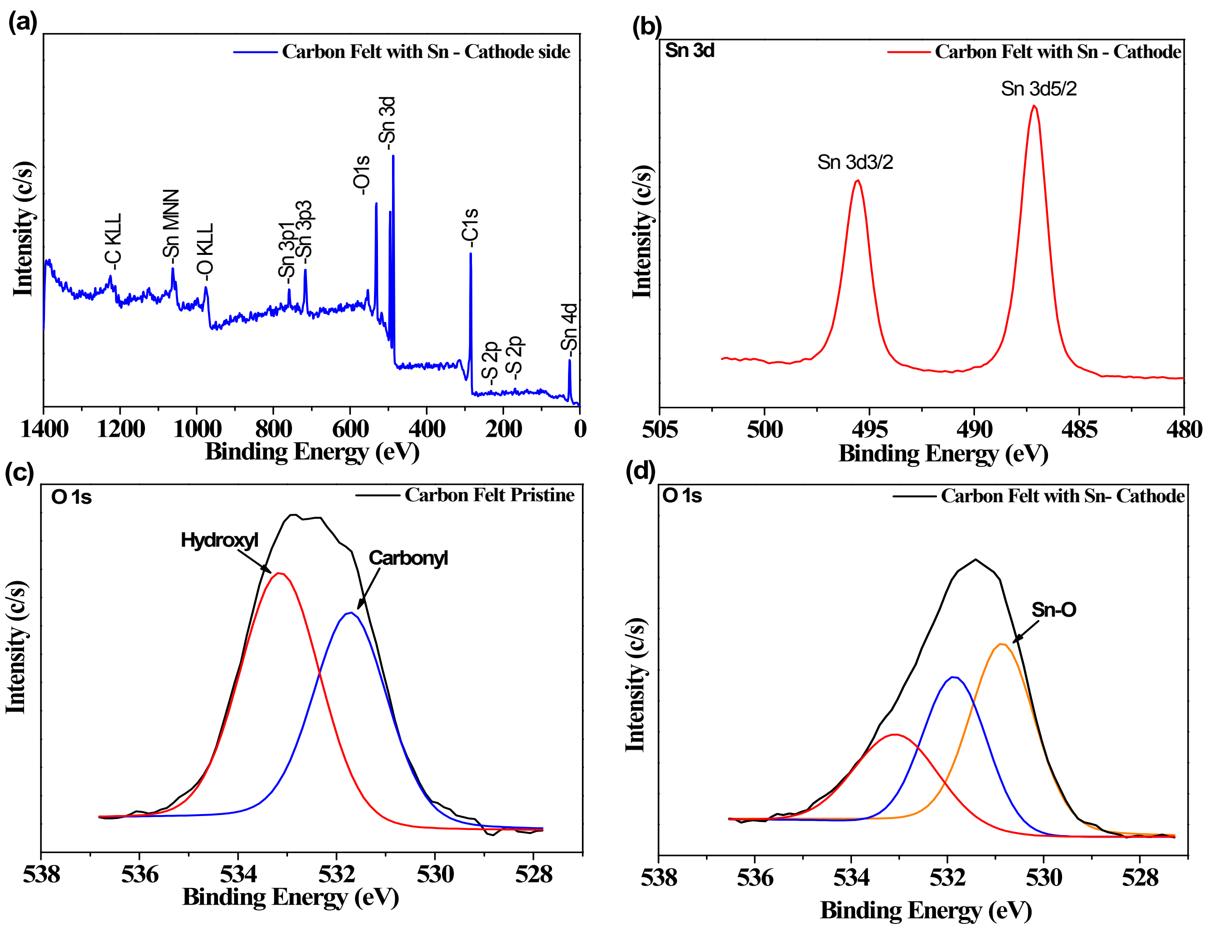

Fig. S8 XPS studies (a) Survey spectrum of cycled CF – cathode side with 0.01 M of Sn^{2+}; (b) Sn 3d core level spectra of (a); (c) O1s spectra of pristine CF; (d) O1s spectra of cycled CF – cathode side with 0.01 M of Sn^{2+} in both anolyte and catholyte.

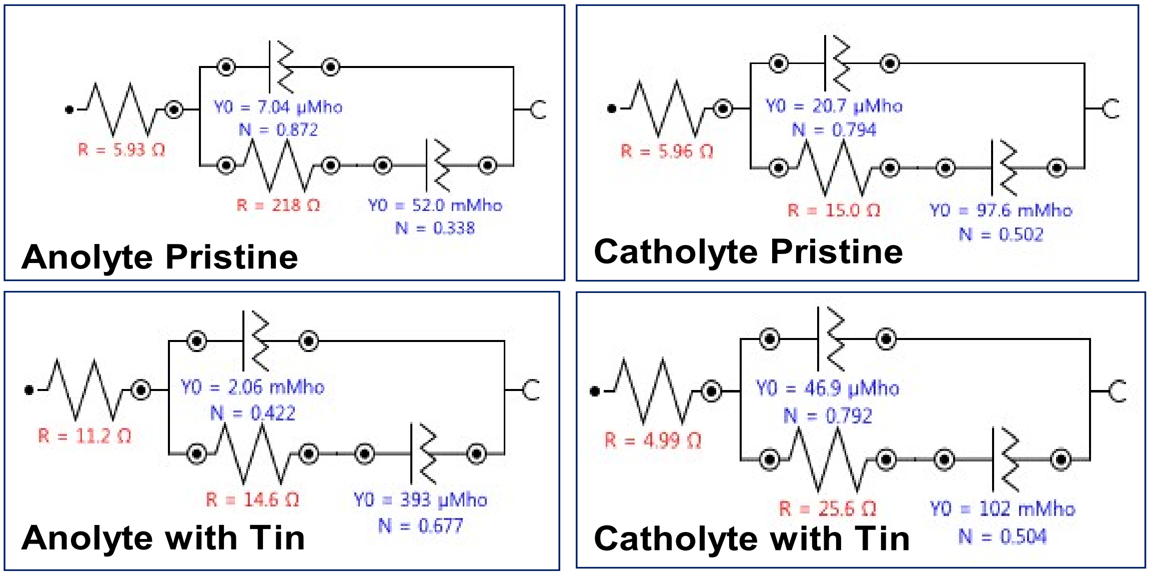

Fig. S9 Equivalent circuits of the fitted Nyquist plots with parameter values for (a,b) pristine electrolyte and (c, d) electrolyte with Sn^{2+} .