Supplementary Material

Highly Stable Titanium-Manganese Single Flow Batteries for Stationary Energy Storage

Lin Qiao [ab], Congxin Xie [b], Mingjun Nan [a], Huamin Zhang [ab], Xiangkun Ma,*[ab] Xianfeng Li,*[b]

[a.] Department of Materials Science and Engineering, Dalian Maritime University, PR China.

[b.] Division of Energy Storage, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China.

1. Experimental Section

Material

Titanium oxysulfate ($TiOSO_4$, Aladdin, 93%), Manganese sulphate ($MnSO_4 \cdot H_2O$, Kermel, >99%), Sulfuric acid (H_2SO_4, 98%) were used without further purification. The Nafion 212 membrane was purchased from Dupont. The electrolytes were prepared with deionized water and filtered out before use.

Electrochemical characterization

Cyclic voltammetry measurement was performed in a three-electrode system on an electrochemical work station (Gamary reference 1000). Graphite plate with the area of 9 cm^2 (3 cm×3 cm) and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. For the positive electrolyte, carbon felt with the area of 1.13 cm^2 (Φ=0.6 cm) was used as working electrode. For the negative electrolyte, graphite plate with the area of 1 cm^2 (1 cm×1 cm) was used as working electrode. Cyclic voltammetry measurement was performed from 0.55 to 1.55 V vs. SCE at a scan rate of 10 mV s^{-1}.

The deposition morphology of sediments

The deposition morphology of sediments on the carbon felt was characterized by scanning electron microscope (SEM, JEOL 6360LV). The samples were dried at room temperature before test. Elemental mappings was tested by energy dispersion spectrum (EDS, Hitachi SU8220 and SU8010).

The characterization of sediments

The sediments were characterized by transmission electron microscope (TEM, FEI Tecnai G2 F30), X-ray diffraction (XRD, PANalytical), X-ray photoelectron spectroscopy (XPS, ThermoFischer, ESCALAB Xi+ with an Al Kα (1486.6eV) X-ray source). For TEM, the samples were acquired by rinsing the carbon felt after charge process and loaded on copper network. For XRD and XPS, the samples were acquired by rinsing, washing and drying at room temperature.

Battery assembly

TMSFBs were assembled by sandwiching Nafion 212 membrane between two carbon felt electrodes according to the previous reports. The volume of the negative electrolyte is 60 mL. And positive electrolyte was sealed in carbon felt, the volume of the positive electrolyte is equal to the pore volume of graphite felt. The negative electrolyte was circulated by magnetic pump with a flow rate of 50-60 ml min^{-1}. In addition, the TMSFB was placed horizontally and positive electrode was at the bottom. Carbon felts were bought from Liaoyang Jingu Carbide Co., Ltd and used without treatment. The effective area of TMSFBs was 6 cm × 6 cm. The electrode thickness of 10 mm or 12 mm was got by overlying two pieces of carbon felts with the thickness of 5 mm or 6 mm, respectively. The electrode compression ratio is listed as Table S1. TMSFBs were terminated by the capacity limit or the upper voltage of 1.6 V for the charging process and a lower voltage of 0.8 V for the discharging. TMSFBs were tested by Neware with a constant current density ranging from 20 mA cm^{-2} to 80 mA cm^{-2}.

2. The calculation for the theoretical capacity and state of charge (SoC).

The theoretical capacity of TMSFB is calculated by the contents of positive active materials.

Table S1. The thickness of the graphite felt and the electrode compression ratio

The thickness of the original graphite felt /mm	The thickness of the graphite felt in the TMSFB [T] (pressing) /mm	The electrode compression ratio
6	4.8	0.8
5	3.8	0.76
10	7.2	0.72
12	9.2	0.77

The porosity of the graphite felt: 90%

The thickness of the graphite felt in the TMSFB (pressing): [T] /mm

The effective area of graphite felt: 6 cm*6 cm

The pore volume of graphite felt (mL): 0.9*6 cm*6 cm*T*10^{-1}

The concentration of $MnSO_4$: [C] /mol L^{-1}

The theoretical capacity of TMSFB (Ah)= 90%*6 cm*6 cm*T*10^{-1}*10^{-3}*C*2*26.8 Ah mol^{-1}

The SOC is calculated by the following formula:

SOC= $\frac{The\ real\ charge\ capacity}{The\ theoretical\ capacity}$

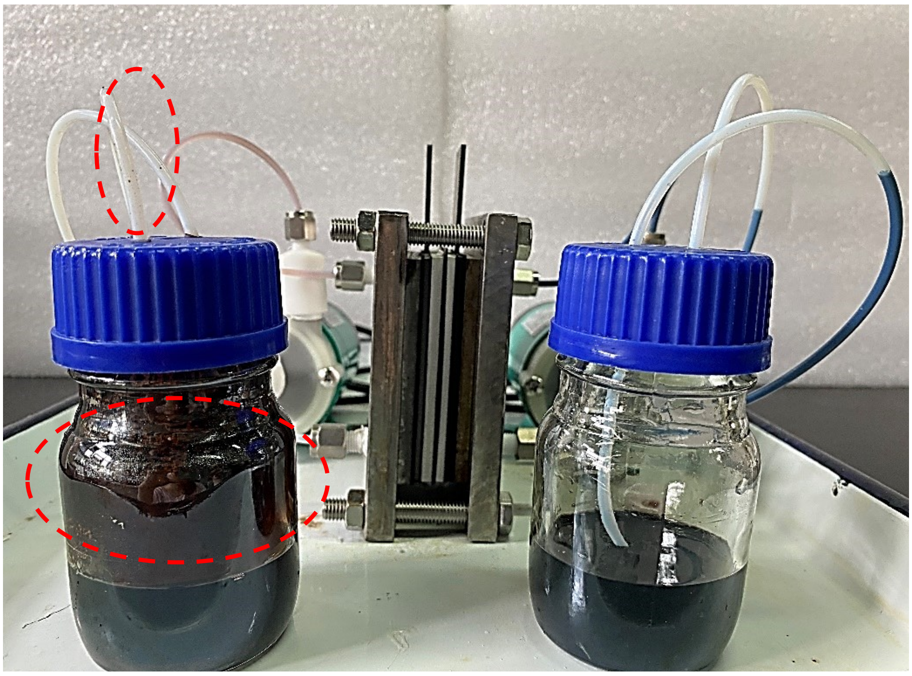

Fig. S1. The optical image of a titanium-manganese flow batteries.

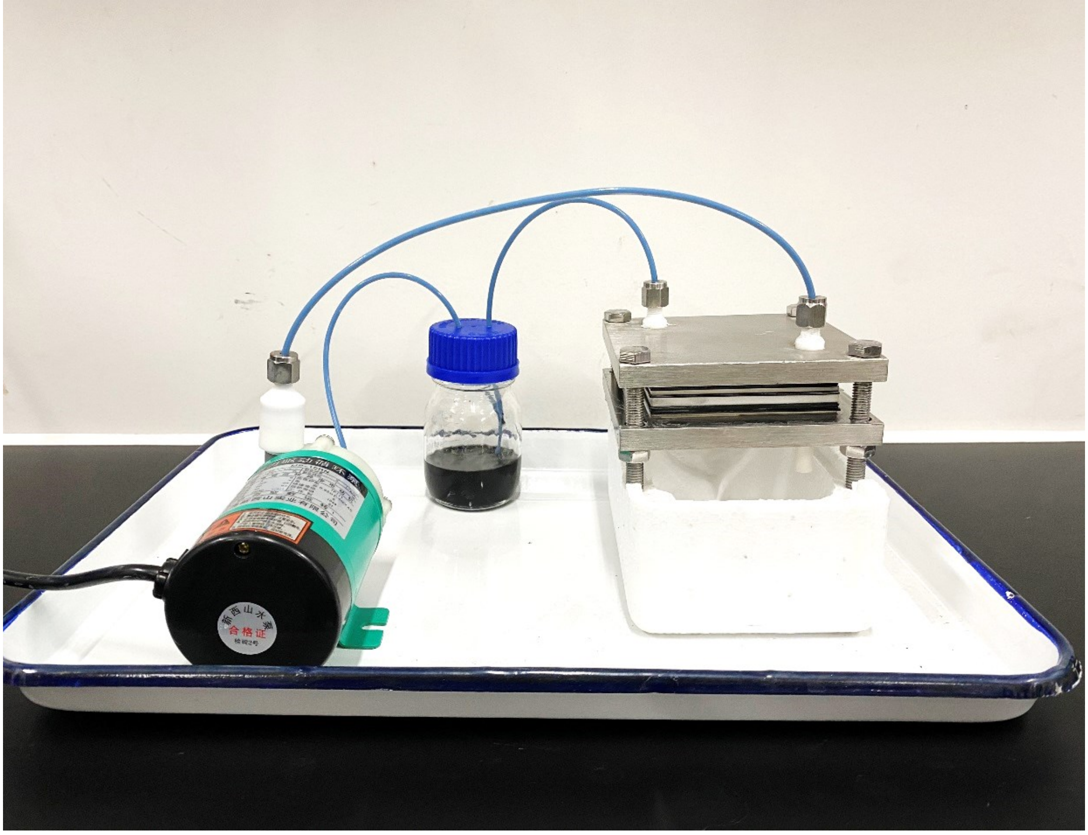

Fig. S2. The optical image of a titanium-manganese single flow batteries (TMSFB).

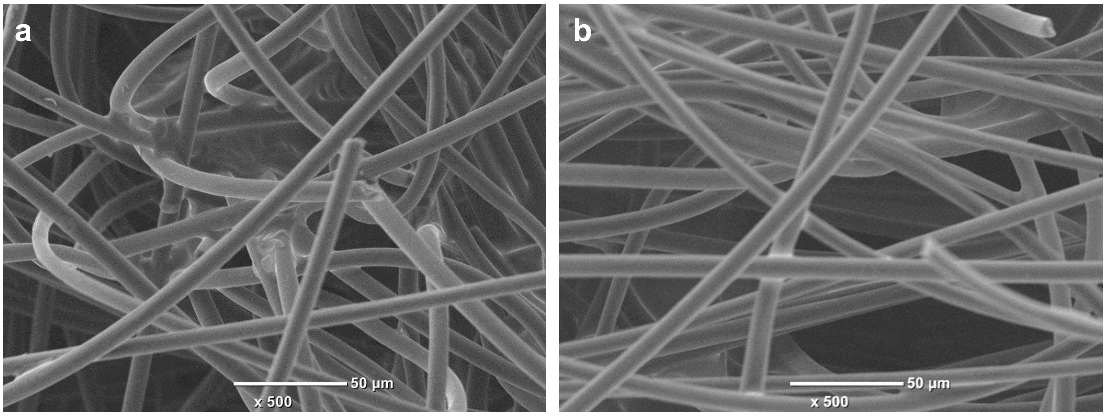

Fig. S3. The morphology of carbon felt electrode (SoC=20%) in TMSFBs with (a) 0.5Mn-3H and (b) 0.5Mn-1Ti-3H.

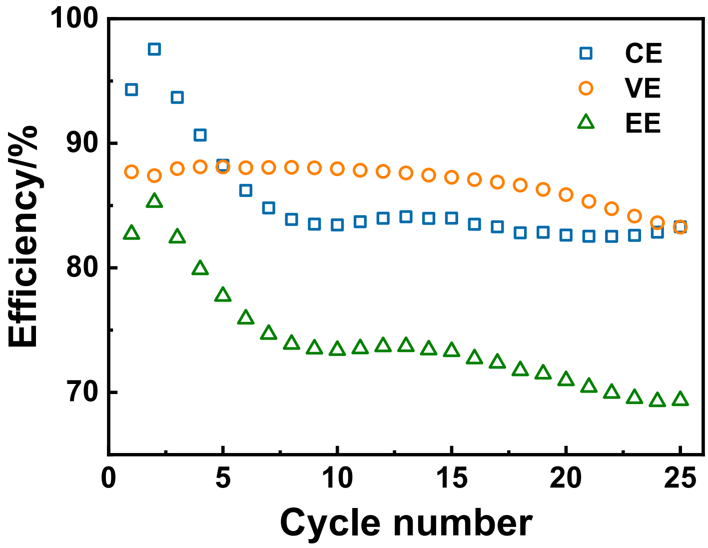

Fig. S4. The performance of a TMSFB with 0.5Mn-3H.

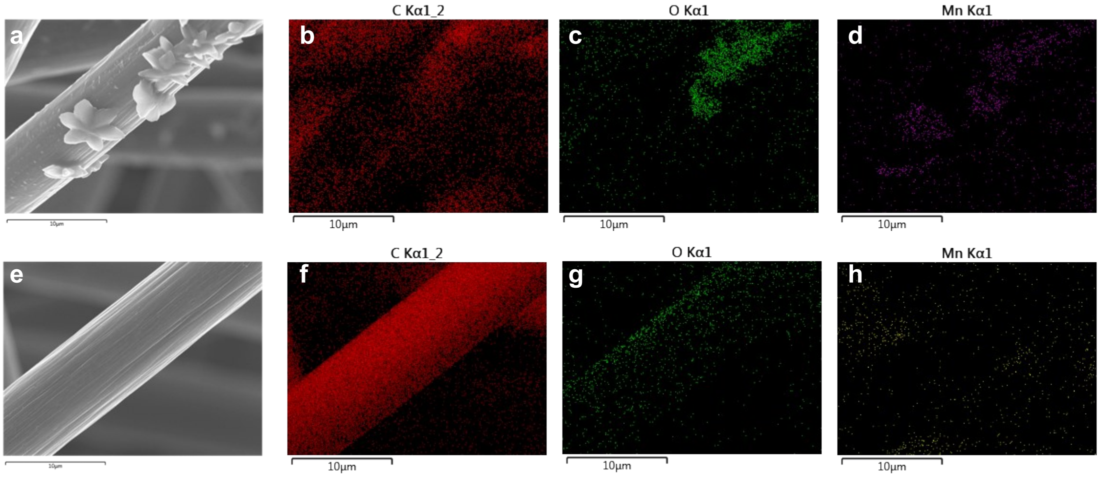

Fig. S5. The SEM images and elemental mappings (C, O, Mn) of carbon felt after the 1st discharge process. (a-d) 0.5Mn-3H, (e-h) 0.5Mn-1Ti-3H.

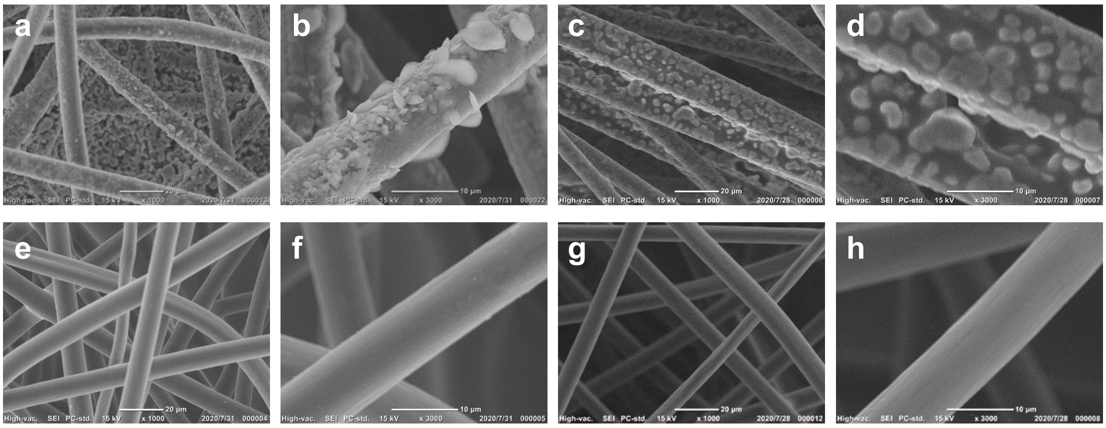

Fig. S6. The morphology of carbon felt electrode in TMSFBs with (a-d) 0.5Mn-3H and (e-h) 0.5Mn-1Ti-3H. (a,b,e,f) Charge to 50% SoC, (c,d,g,h) Discharge to 50% SoC.

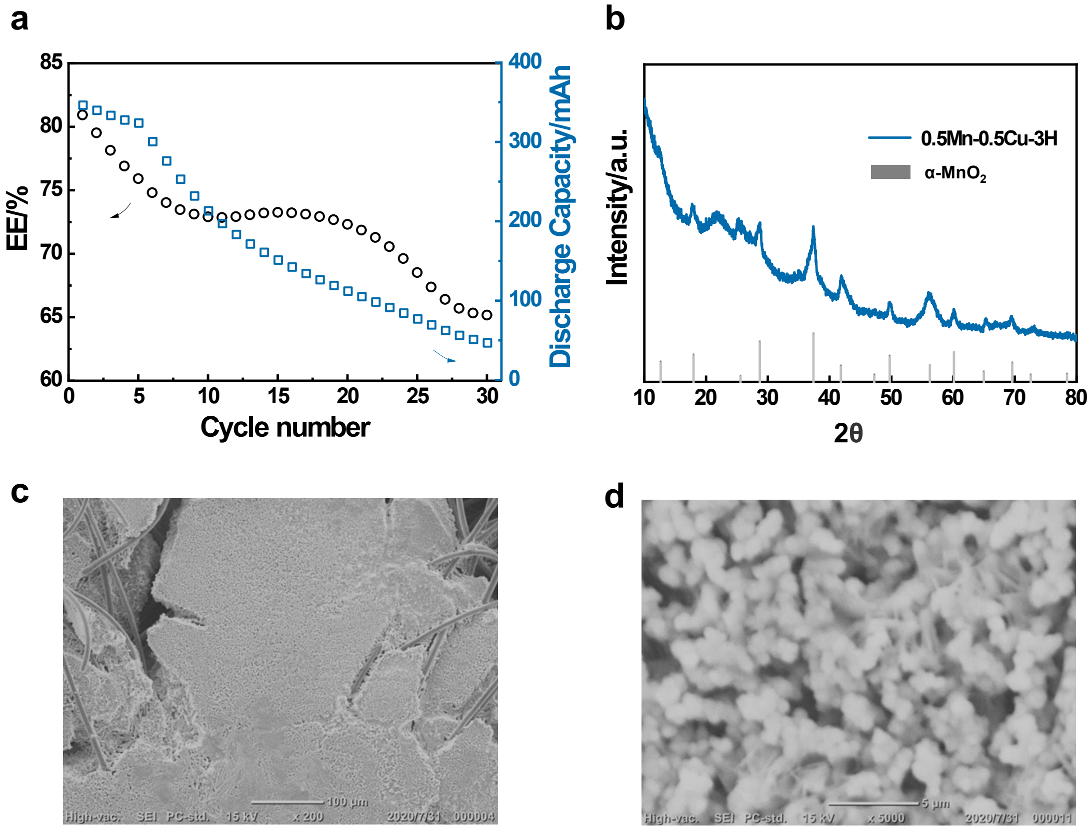

Fig. S7. (a) The cycle life of TMSFBs with 0.5Mn-0.5Cu-3H. (b) The XRD patterns of sediments from TMSFBs with 0.5Mn-0.5Cu-3H after charging. (c, d) The SEM images of carbon felt surface in a TMSFB with 0.5Mn-0.5Cu-3H after 100th cycle.

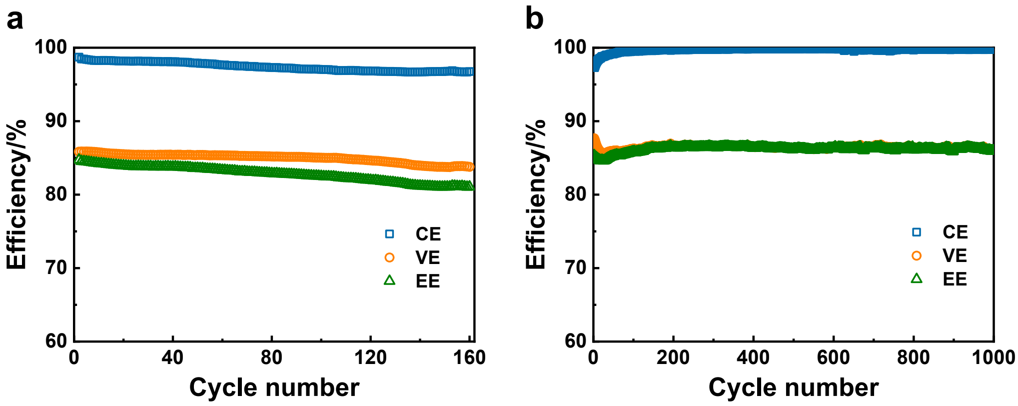

Fig. S8. The performance of TMSFBs with (a) 0.5Mn-1Ti-2H, (b) 0.5Mn-1Ti-4H.

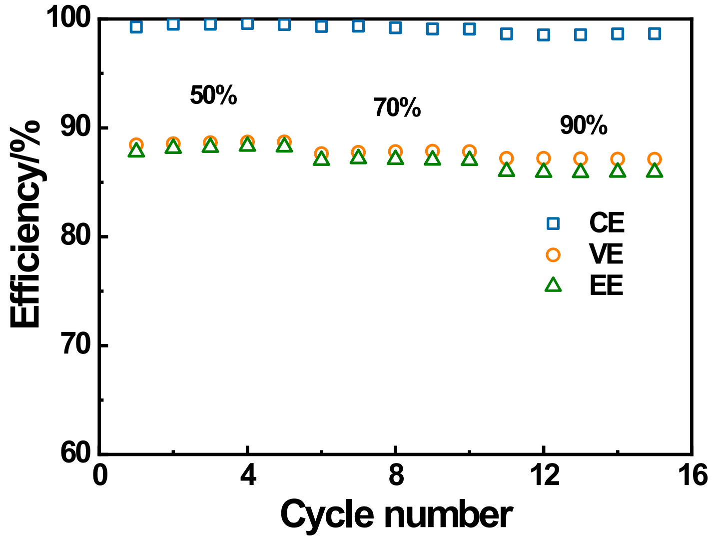

Fig. S9. The performance of TMSFBs with SoC (50%, 70%, 90%) at the current density of 40 mA cm^{-2}.

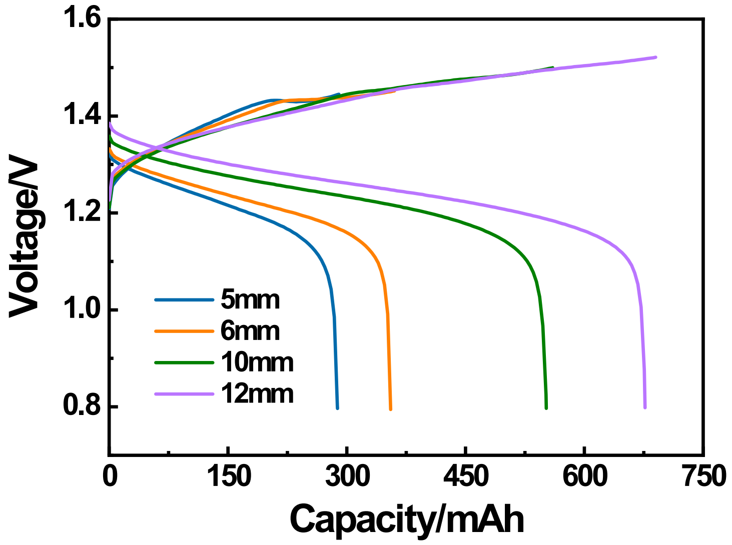

Fig. S10. The charge-discharge profiles of TMSFBs with different electrode thickness (5, 6, 10, 12 mm) at the current density of 40 mA cm^{-2}.

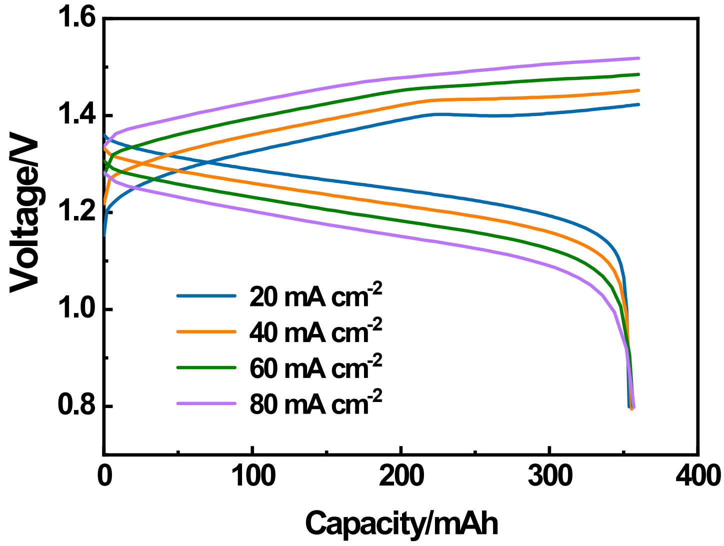

Fig. S11. The charge-discharge profiles of TMSFBs at the current density of 20, 40, 60, 80 mA cm^{-2}.

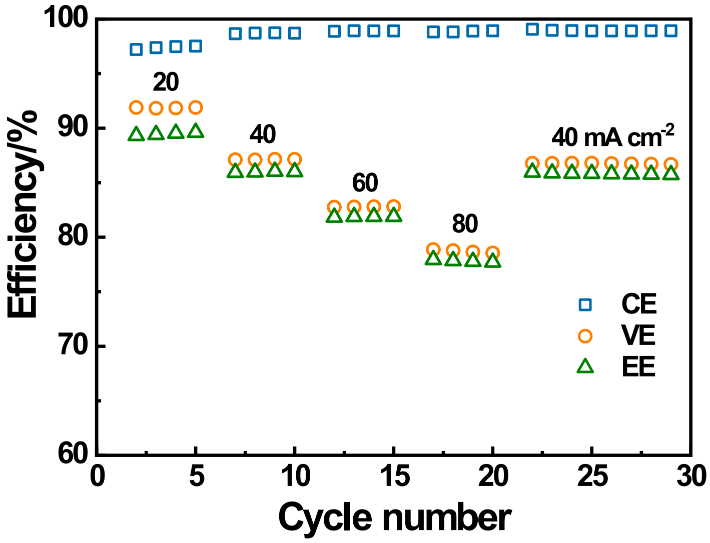

Fig. S12. The rate performance of a TMSFB with 1Mn-1Ti-3H (Area capacity=20 mAh cm^{-2}).

Table S2. The solution composition of xMn-yTi-zH electrolyte.

Sample	The concentration of $MnSO_4$/moL L^{-1}	The concentration of $TiOSO_4$/moL L^{-1}	The concentration of H_2SO_4/moL L^{-1}
0.5Mn-3H	0.5	0	3
0.5Mn-1Ti-3H	0.5	1	3
0.5Mn-1Ti-2H	0.5	1	2
0.5Mn-1Ti-4H	0.5	1	4
1Mn-1Ti-3H	1	1	3

Table S3. XPS spectra resolving results of the sediments from TMSFBs with 0.5Mn-3H and 0.5Mn-1Ti-3H after charging.

Binding energy/eV	$Mn2p^{1/2}$	$Mn2p^{3/2}$	$\triangle E_{Mn2p}$	Mn3s	Mn3s	$\triangle E_{Mn3s}$	$Ti2p^{1/2}$	$Ti2p^{3/2}$	$\triangle E_{Ti2p}$
0.5Mn-3H	654.1	642.8	11.4	88.56	83.76	4.8			
0.5Mn-1Ti-3H	654.2	642.8	11.4	88.66	83.86	4.8	464.2	458.5	5.7