

Electronic Supplementary Information (ESI)

Tin Dioxide as a High-Performance Catalyst towards Ce(VI)/Ce(III) Redox Reaction for Redox Flow Battery Applications

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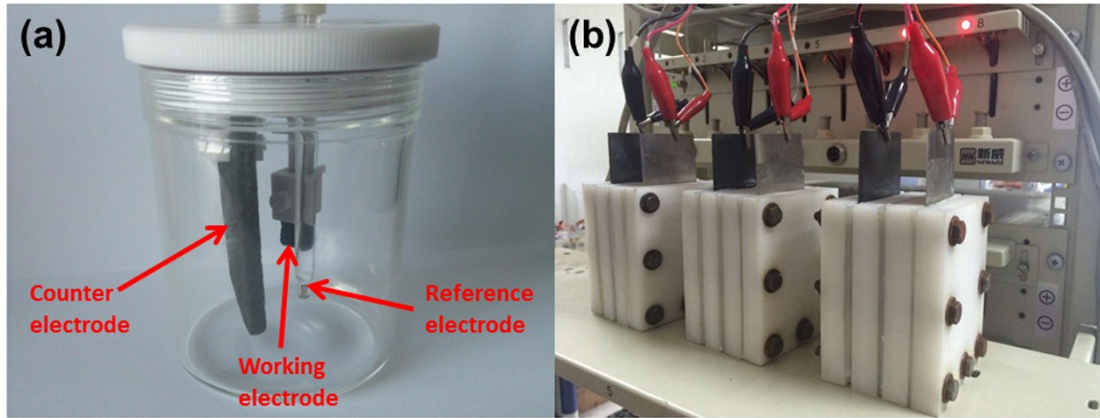


Fig. S1. Digital photograph of (a) the three-electrode electrochemical cell and (b) the actual test rig being tested.

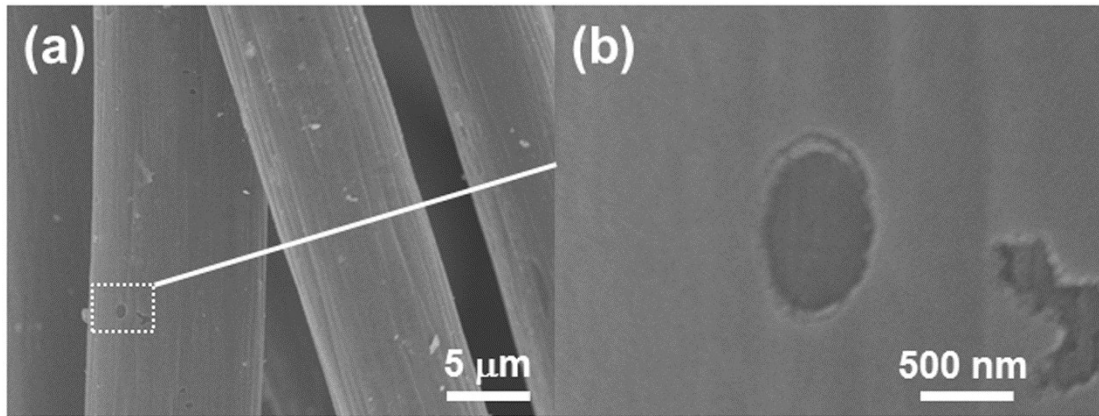


Fig. S2. SEM images of the GFSN electrodes.

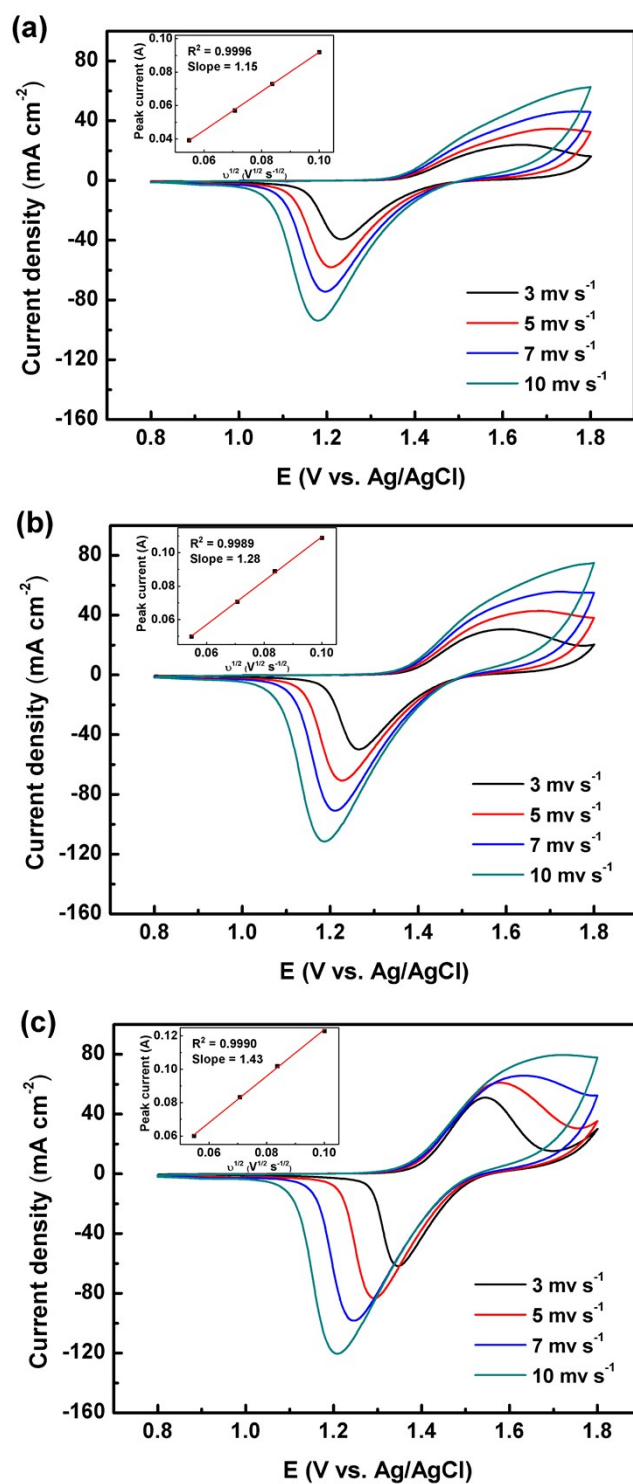


Fig. S3. CV curves of the (a) GF, (b) AGF and (c) GFSN electrodes in 0.05 M Ce(III) methanesulfonate + 1.0 M MSA electrolyte from 0.8 V and 1.8 V vs. Ag/AgCl under various scan rate. Insets: the plot of the peak current vs. the square root of each scan rate.

S1. The electrochemical surface area (ECSA)

The electrochemical surface area (ECSA) that is available for the electron transfer to/from the species contained in solution can be estimated from the Randles-Sevcik equation. This equation relates the peak current with the square root of the scan rate, as follows:

$$i_p = 2.99 \times 10^5 n (\alpha n)^{1/2} A D_0^{1/2} C_0 \nu^{1/2}$$

where i_p is the peak current, n is the number of electrons participating in the reaction, α is the transfer coefficient (0.5), A is the ECSA (cm^2), C_0 is the initial concentration of the electroactive species (mol cm^{-3}), D_0 is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and ν is the scan rate (V s^{-1}). The values of the diffusion coefficients were obtained from bibliography (S1),

$0.69 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

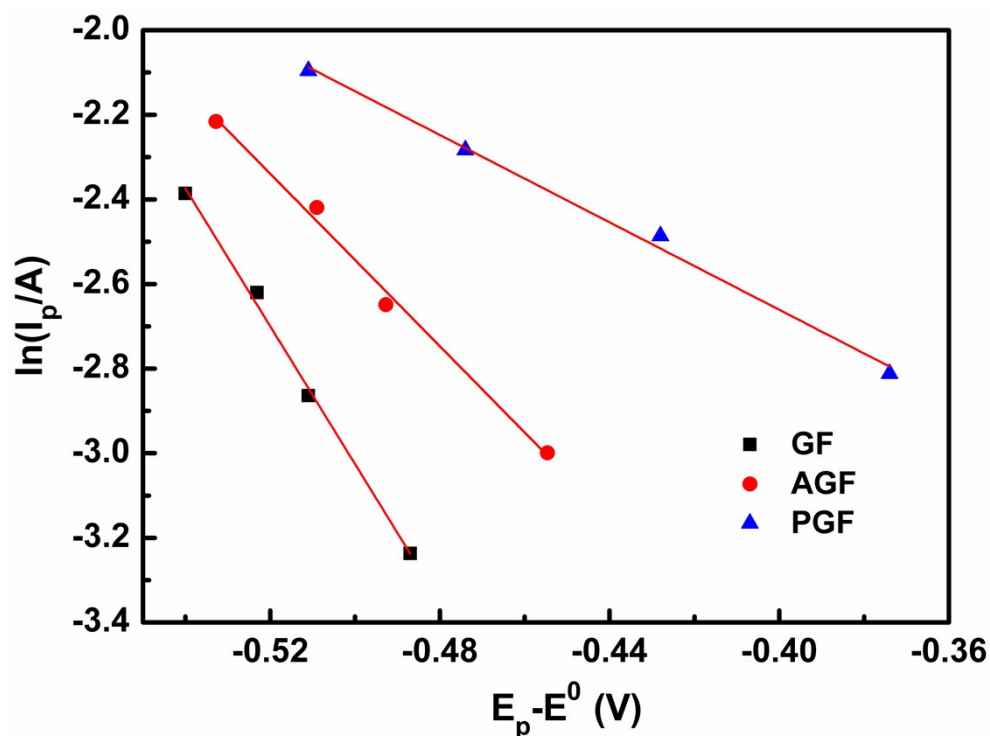


Fig. S4. Comparison of standard rate constant (k) for GF, AGF and PGF.

S2. The standard rate constant, k_0

The peak current in the CV curves (Fig. S3) can be described by the following equation for a totally irreversible reaction:

$$i_p = 0.227nFAC_0k_0 \exp\left[\frac{-\alpha nF(E_p - E^0)}{RT}\right]$$

where i_p is the peak current, n is the number of electrons participating in the reaction, F is the Faraday constant, A is the active surface area of the electrode, C_0 is the initial concentration of the electroactive species, α is the transfer coefficient (0.5), E_p is the peak potential, E^0 is the standard electrode potential, R is the gas constant, and T is the temperature.

According to this equation, a plot of $\ln(i_p)$ vs. $E_p - E^0$, should yield a straight line with a slope of $-\alpha nF/(RT)$, and an intercept proportional to k_0 , from which k_0 values can be calculated (Fig. S4).

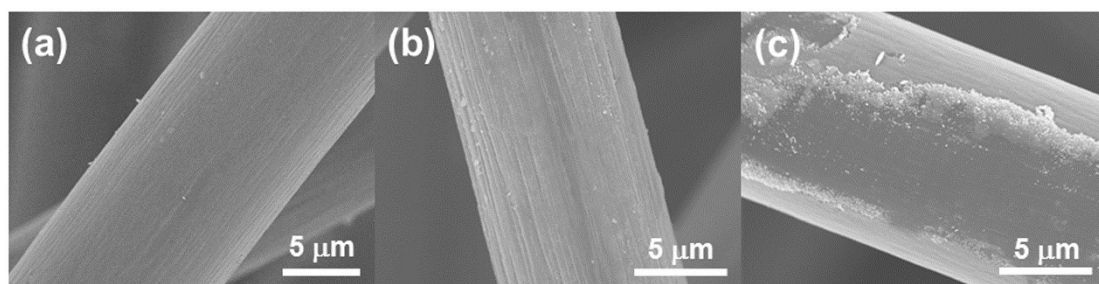


Fig. S5. SEM images of various GFSN samples with with different heat treatment temperatures (a) 500 °C, (b) 600 °C and (C) 700 °C.

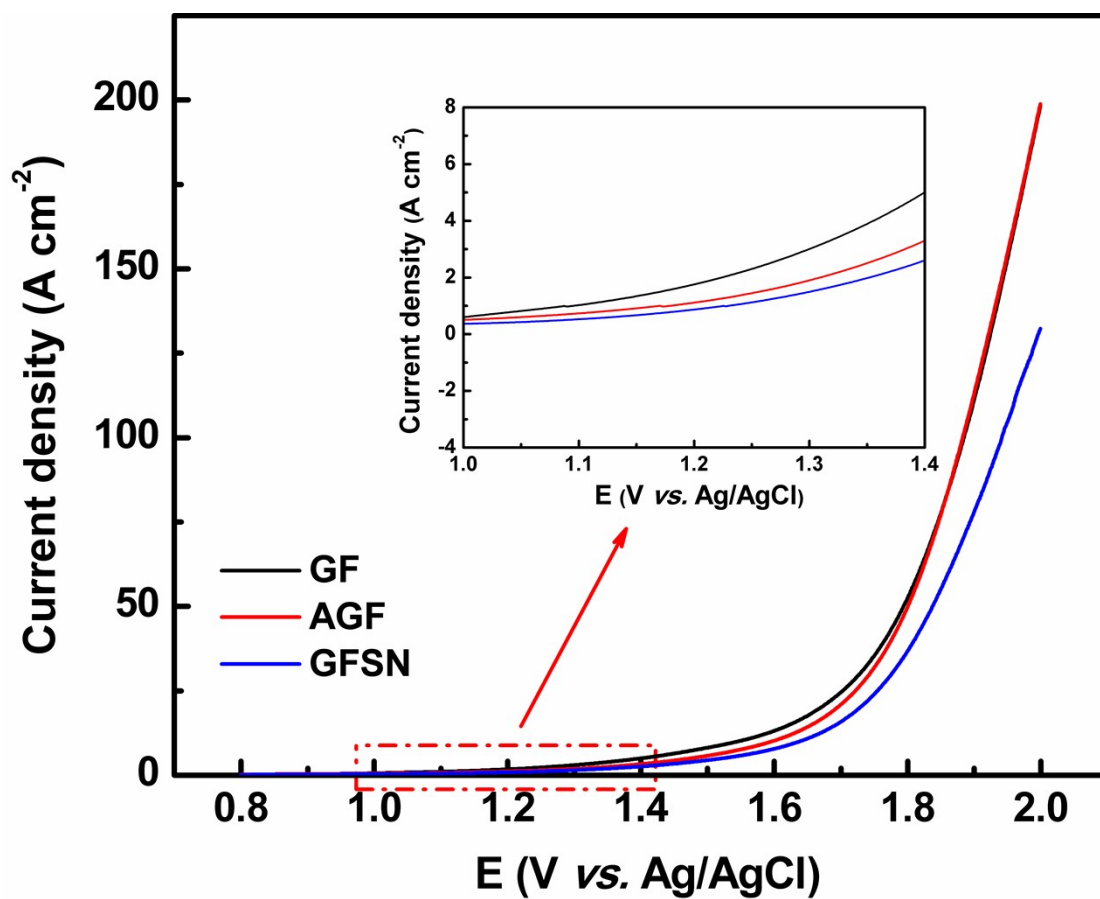


Fig. S6. LSVs performed in the electrolytes of 1.0 M MSA without cerium salts from 0.8 V and 2.0 V at $10\ mV\ s^{-1}$.

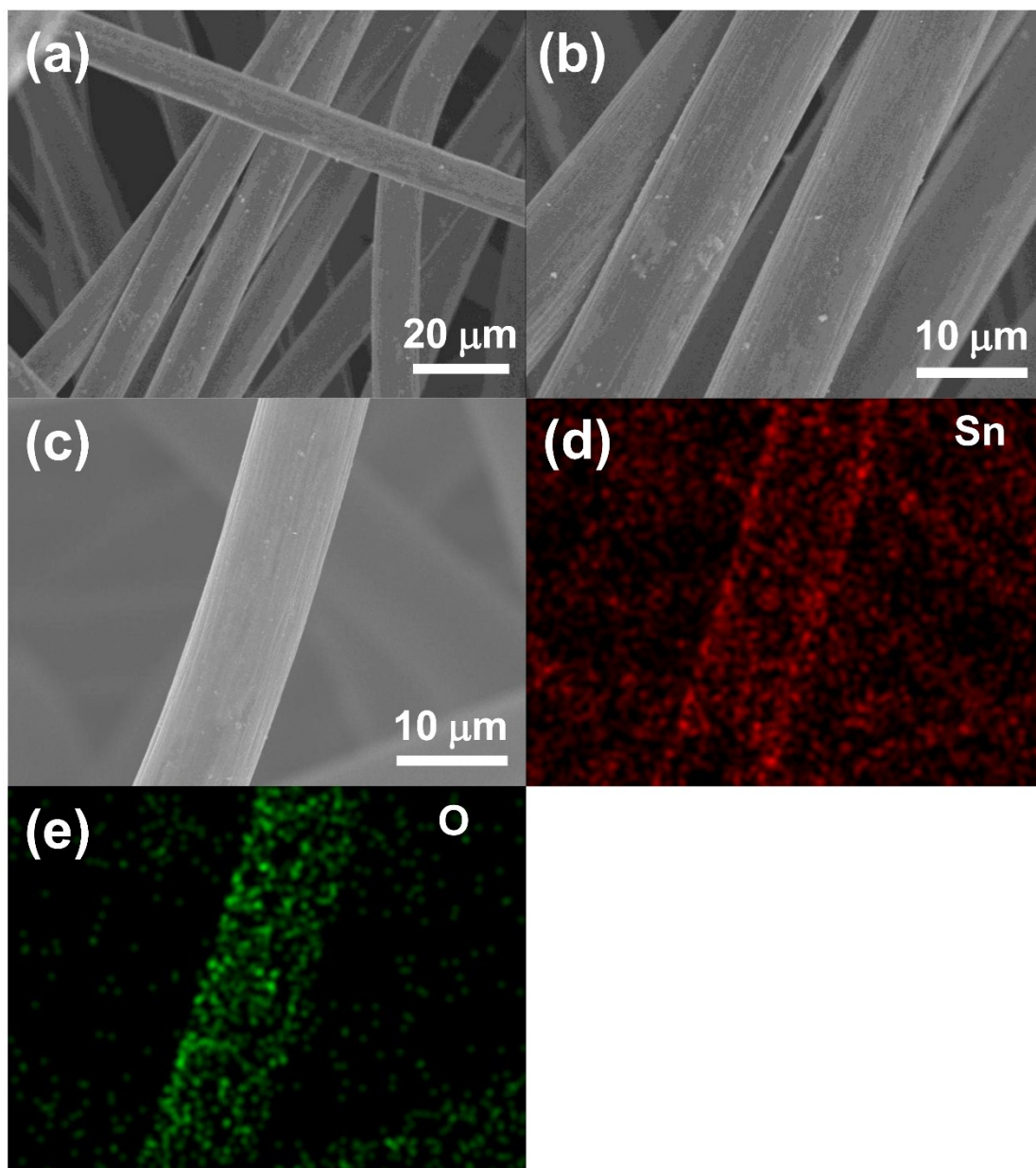


Fig. S7. (a)-(b) SEM images and (c)-(e) corresponding EDS mapping of the SnO₂ catalyst coated graphite felt electrode after 100 charge/discharge cycles.

Supplementary Reference

- (S1) P. K. Leung, C. Ponce de Le' on, C. T. J. Low and F. C. Walsh,
Electrochim. Acta, 2011, **56**, 2145–2153.