

Supplementary information

Dynamic Hydrogen Bubble Template Electrodeposited Bi on Graphite Felt and the Effect of its Post-processing in Vanadium Redox Flow Batteries

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DHBT method with and without Bi electrodeposition

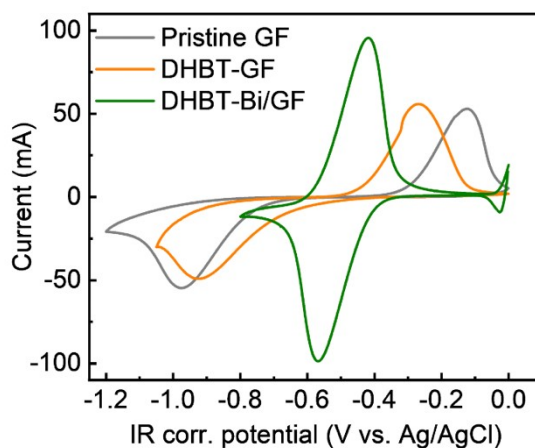


Figure S1. CV curves of pristine GF, DHBT-GF and DHBT-Bi/GF at a scan rate of $4 \text{ mV}\cdot\text{s}^{-1}$ with a 3-electrode setup in $0.16 \text{ M V}^{3+}/\text{V}^{2+}/2 \text{ M H}_2\text{SO}_4$ electrolyte.

In order to verify the catalytic effect of Bi, the influence of the DHBT procedure itself, namely, applying the same negative potential for the same period of time using the same concentration of supporting electrolyte 2 M HNO_3 but without Bi, has been studied. From the CV curves, it can be observed that the peak separation is closer after the DHBT without Bi treatment than that of a pristine GF. It could be inferred that the polarization of GF to negative potentials could induce corrosion and H_2 bubbles roughen the felt surface which leads to slightly better performance. However, when this “blank” sample is compared to the sample with Bi electrodeposition, the enhancement in either kinetics or redox pair conversion rate appears to be negligible.

Bi electrodeposition on GC

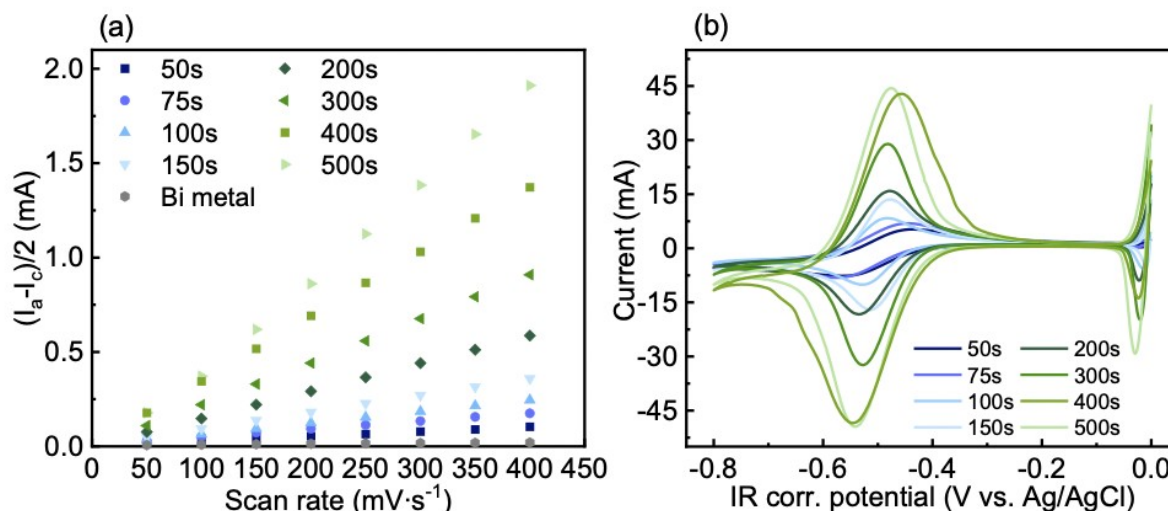


Figure S2. (a) Dependence of double layer charging current on scan rate at a potential of 0.4 V vs. Ag/AgCl; (b) CV curves of GCs with different Bi electrodeposition time.

Table S1. Summary of the DLC, ECSA, peak current, and normalized current density of Bi/GCs with different electrodeposition time.

Electrodeposition Time (s)	50	75	100	150	200	300	400	500
Capacitance (μF)	250	418	603	887	1460	2290	3430	5020
ECSA (cm^2)	1.25	2.1	3.03	4.46	7.34	11.51	17.24	25.23
$I_{\text{cathodic peak}} / I_{\text{anodic peak}}$ (mA)	-7.65/5.26	-8.148/6.92	-10.06/8.58	-17.13/13.58	-18.29/16.03	-32.38/28.86	-48.47/42.83	-49.47/44.40
Norm. current density ($\text{mA}\cdot\text{cm}^{-2}$)	-6.12/4.21	-3.88/3.29	-3.32/2.83	-3.84/3.04	-2.49/2.18	-2.81/2.51	-2.81/2.48	-1.96/1.76

As shown in Figure S2 (a) and Table S1, until an electrodeposition time of 500 s, the following relation holds true: the longer the electrodeposition time, the higher the corresponding capacitance and ECSA. The CV curves in Figure S2 (b) show that the $\text{V}^{3+}/\text{V}^{2+}$ redox reaction is reproducible, and the corresponding current is proportional to the ECSA. The result shows that the normalized current density is the highest when the electrodeposition time is 50 s. However, the relatively larger peak separation in the CV curve indicates that the GC was not fully covered with Bi foam. According to the trend in Table S1, to fully cover the GC with the size of 1 cm^2 , at least 100 s deposition time is required. On the other hand, the deposition time should not be too long as well, or the amount of deposited Bi could be too high and subsequently peel off the GC. From the normalized current summarized in Table S1, it could be inferred that the most efficient deposition time range is between 150 s and 400 s.

Bi electrodeposition on GF

Following the investigations with 2-D structured GCs, the optimization experiments were carried out with porous structured GFs employing the same characterization method as described above. A higher magnification SEM image of nano-structural Bi on GFs in Figure S3 (a) shows the effectiveness of the DHBT electrodeposition on 3D substrates.

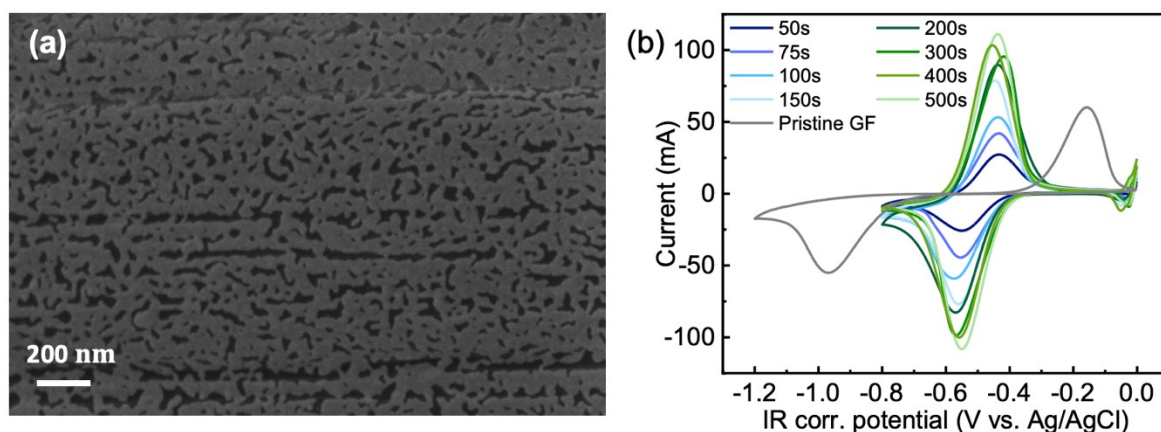


Figure S3. (a) A higher magnification SEM image of electrodeposited Bi by DHBT method on GF. (b) CV curves of Bi/GFs with different electrodeposition time.

Table S2: Summary of the DLC, ECSA, peak current, and ECSA normalized current density of Bi/GFs with different electrodeposition time.

Electrodeposition Time (s)	50	75	100	150	200	300	400	500
Capacitance (μF)	526	608	578	547	588	608	649	716
ECSA (cm^2)	2.64	3.05	2.90	2.74	2.95	3.05	3.26	3.60
$I_{cathodic\ peak} / I_{anodic\ peak}$ (mA)	-25.77/ 27.29	-44.53/ 41.96	-59.13/ 53.23	-76.91/ 78.71	-82.81/ 89.7	-98.70/ 95.55	-100.1/ 103.4	-108.2/ 111.1
Norm. current density ($mA \cdot cm^{-2}$)	-9.76/ 10.34	-14.6/ 13.76	-20.39/ 18.36	-28.07/ 28.73	-28.07/ 30.41	-32.36/ 31.33	-30.71/ 31.71	-30.05/ 30.86

The peak currents of the vanadium redox reaction increase continuously with the electrodeposition time reflecting the catalytic effect of Bi for V^{3+}/V^{2+} redox reactions, as shown in Figure S3 (b). The normalized current density is the highest when the deposition time is 300 s. DLC, ECSA, peak current, and ECSA normalized current density of Bi/GFs with different electrodeposition time are all summarized in Table S2.

Brunauer-Emmett-Teller (BET) surface area analysis

The measured BET surface areas of a pristine GF, DHBT Bi/GF under air drying, and DHBT Bi/GF under vacuum drying are $0.4984\ m^2 \cdot g^{-1}$, $1.3959\ m^2 \cdot g^{-1}$, and $0.7831\ m^2 \cdot g^{-1}$, respectively. The BET surface area results do not show significant improvement after the Bi electrodeposition. Compared to the ECSA results listed in Table S1 and Table S2 which are derived by correlating the double layer capacitance (DLC) to the active surface area, it can be confirmed that the ECSA is increased after the Bi electrodeposition, although the BET surface area increase is not that high, which indirectly also reflects the catalytic effect of Bi.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) characterization on the amount of Bi before and after the stability test

The ICP-OES result shows that the total amount of the deposited Bi on GF after 300 s electrodeposition is 6.5 mg. According to the synthesis parameters at constant current -0.1 A for 300 s, it can be concluded that during the synthesis about 30% of the charge flows into the Bi^{3+} electrodeposition, while 70% is used for the hydrogen reduction reaction acting as a dynamic template. After 200 CV cycles, the GF and the electrolyte were recovered from the electrolyte for

ICP-OES tests. It shows that the total amount of Bi on the GF after 200 cycles is 2.3 mg and the amount of Bi in the electrolyte is 1.2 mg which is smaller than the total amount of Bi on a freshly prepared GF. There are several reasons for the loss of Bi: 1. The pre-wetting process by injection on GF can cause some of the larger Bi particles to lose contact to the substrate and fall off; 2. Some larger Bi agglomerates may settle down to the bottom of the vanadium solution 3. Before the ICP-OES test, to dissolve the GF better, it is grinded with mortar and pestil resulting in some material being attached to the mortar and pestil.