Supporting 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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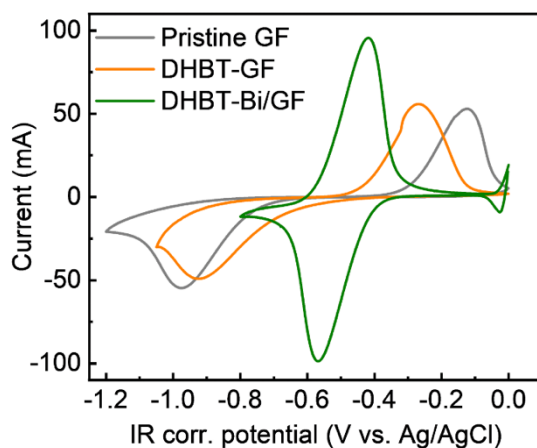## DHBT method with and without Bi electrodeposition

Figure S1. CV curves of pristine GF, DHBT-GF and DHBT-Bi/GF at a scan rate of 4 mV·s^{-1} with a 3-electrode setup in 0.16 M V^{3+}/ V^{2+}/ 2 M H$_2$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 a relatively better performance. However, when it is compared to the sample with Bi electrodeposition, the enhancement in either kinetics or redox pair conversion rate appears to be negligible.
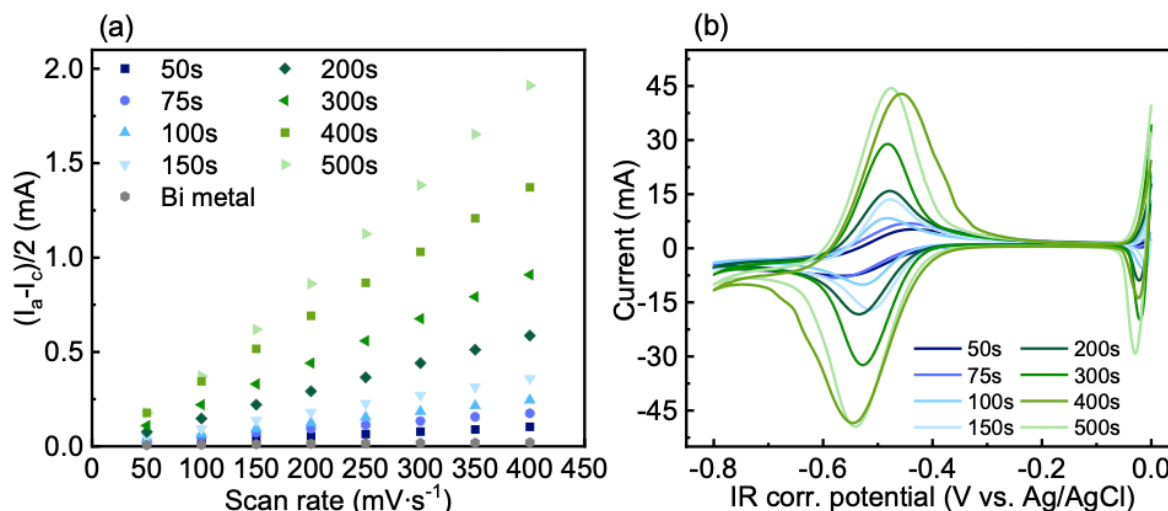
Bi electrodeposition on GC

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
$I_{cathodic\ peak}$ / $I_{anodic\ peak}$ (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 (mA·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) (b) 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 (c) show that the V^{3+}/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 shows 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 deposited Bi could be too much for the GC to hold. 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.
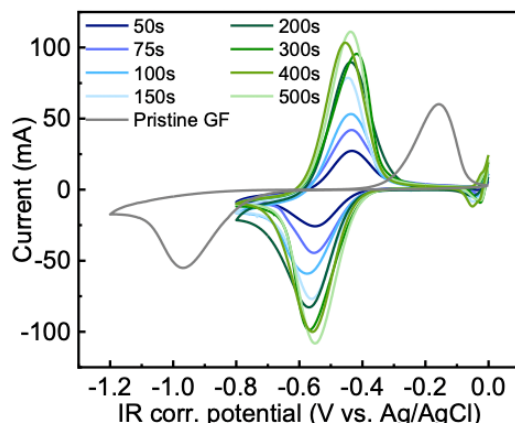
Figure S3. CV curves of Bi/GFs with different electrodeposition time.

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·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 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. 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.

ICP-OES characterization on the amount of Bi before and after 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 settings at constant current -0.1 A for 300 s, it can be inferred 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 taken 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 down; 2. Some Bi big agglomerations drop into the bottom of the vanadium solution 3. Before ICP-OES test, to dissolve the GF better, it is grinded with mortar and pistil resulting in that some Bi are attached on the mortar and pistil.