Modified Graphite Felt Electrodes for Iron-Chromium Redox Flow Batteries

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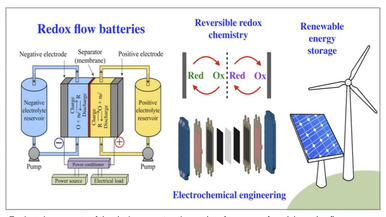
Abstract

Vanadium flow batteries (VFBs) are currently the most commercially advanced flow battery (RFB) technology. However, the high cost and scarcity of vanadium limit the widespread adoption and further cost reduction of VFBs. In contrast, iron-chromium flow batteries (ICFBs) have garnered attention due to their lower cost, wide operational temperature range, and environmental compatibility. Despite these advantages, the performance of ICFBs is hindered by the limited electrochemical activity and poor hydrophilicity of conventional graphite felt (GF) electrodes, which reduce the number of active reaction sites. Moreover, the sluggish Cr^{3+}/Cr^{2+} redox kinetics compared to Fe^{2+}/Fe^{3+} and the tendency for hydrogen evolution side reactions further diminish battery efficiency. In this study, we employed KOH as an etching agent to improve the electrochemical properties of GF by introducing micropores and oxygen-containing functional groups on its surface, thereby enhancing its hydrophilicity and active site availability. Additionally, nanomaterials synthesized using supercritical fluid (SCF) technology were uniformly deposited onto the GF surface to further increase the specific surface area of the electrodes. Comprehensive structural analyses, including Raman spectroscopy, X-ray diffraction, scanning electron microscopy, and specific surface area measurements, were conducted to evaluate the effects of these modifications. The electrochemical performance of the modified GF electrodes was characterized using electrochemical impedance spectroscopy and cyclic voltammetry. Furthermore, single-cell tests were performed to assess the overall performance enhancements in ICRFB systems using the modified electrodes.

Introduction

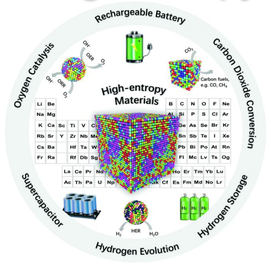
Flow battery (FB)

- Stores energy in liquid electrolytes that flow through the battery during charge and discharge.
- Easy to scale up, safe, Fast charging and discharging.
- Flow batteries offer high safety and long lifespan, making them suitable for diverse energy management applications such as renewable energy storage, smart grids, and microgrids.



Engineering aspects of the design, construction and performance of modular redox flow batteries for energy storage. *Journal of Energy Storage*, **2017**, *11*, 119–153.

High entropy oxides (HEOs)



- HEOs are oxide materials composed of five or more metallic elements in equimolar ratios along with oxygen.
- They typically exhibit a single-phase solid solution structure, such as rock-salt, spinel, or perovskite types.
- High-entropy oxides feature stable single-phase structures, excellent overall stability, and high catalytic activity due to abundant active sites and tunable properties.
- Commonly used in solid electrolytes and electrode materials for lithium/sodium-ion batteries, fuel cells, catalysts, thermoelectric, and magnetic materials.

High-entropy energy materials: challenges and new opportunities. *Energy Environmental Science*, **2021**, *14*, 2883.

Challenges

- **Poor reaction kinetics** of the Cr^{3+}/Cr^{2+} redox couple → reduces power density.
- **$Cr(OH)_3$ precipitation** during the reduction process → shortens cycle life.
- **Low redox potential** of the Cr^{3+}/Cr^{2+} couple → susceptible to hydrogen evolution reaction (HER), lowering energy efficiency.
- **Low energy density** (~20 Wh/L) compared to vanadium flow batteries (~30 Wh/L).
- **High overpotential** → limits voltage efficiency.

Research Highlights

This study aims to develop a high-performance iron-chromium flow battery by optimizing electrode modification materials.

1. Developing high-performance ICFB by improving felt electrodes.
2. Synthesis of high-performance materials using supercritical fluids for modification of negative electrodes.

Experimental Procedures

KOH treatment

GFs were immersed in high concentration KOH solution to form a uniform KOH crust on the surface of GF fibers, followed by vacuum drying at 60 ˚C for 12 h. Afterwards, the KOH-treated GFs were calcined at 600 ˚C for 2 h. All the procedures were operated under N_2 atmosphere in a horizontal furnace. The resulting etched GFs (GF-10) were rinsed thoroughly with diluted HCl and deionized water to eliminate the residual potassium species.

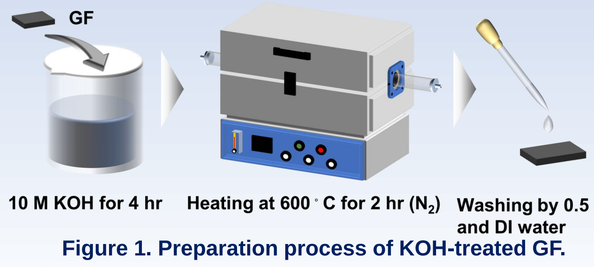


Figure 1. Preparation process of KOH-treated GF.

Synthesis of HEO

HEOs were synthesized via CO_2 supercritical hydrothermal processing using a nitrate solution containing five transition metal precursors—Cr, Mn, Fe, Co, and Ni. The metal precursor suspension was heated at 70 ˚C for 2 h, followed by centrifugal filtration and a rinse with ultrapure water. Then, it was calcined at 900 ˚C for 2 hours in air atmosphere.

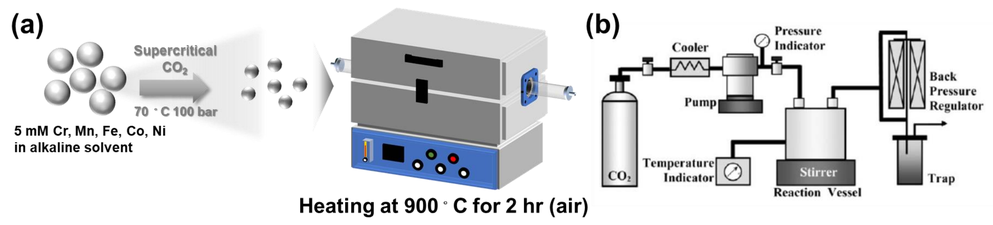


Figure 2. Preparation process of HEOs (a).Schematic diagram of supercritical hydrothermal method.

ICFB cell tests

The ICFB cell measurements were performed in a solution containing 0.5 M $FeCl_2$ + 0.5 M $CrCl_3$+0.005 M Bi_2O_3 at a potential range of 0.2–1.4 V. Unmodified KOH-GF and HEO-decorated KOH-GF were employed as the positive and negative electrodes (area = 3 cm × 3 cm), respectively. An ion-exchange membrane, specifically Nafion 117, was utilized in the setup. The volume of electrolyte storage chambers on both sides was 40 mL, circulating separately using two pumps at 30 mL min^{-1}.

Results and disscussion

1 KOH-Treated Graphite Felt

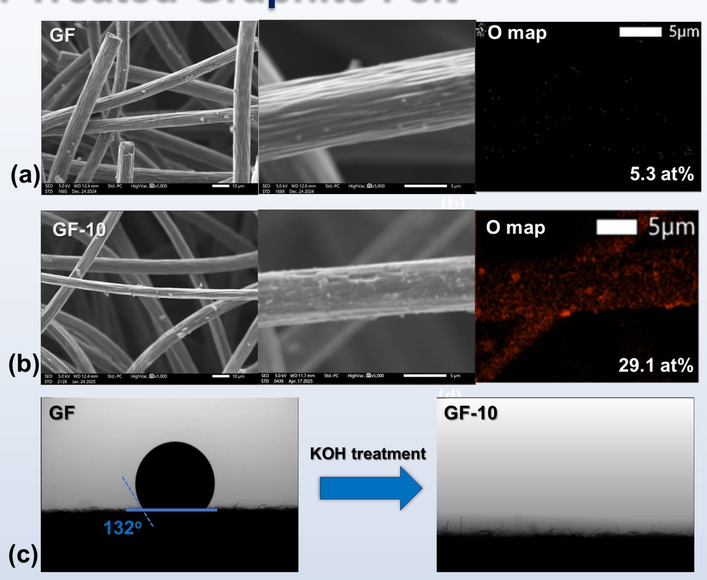


Figure 3. SEM and EDX images of GF (a) and GF-10 (b), and the contact angle of electrolyte droplets on GF and GF-10 surfaces (c).

2 Identification of HEO

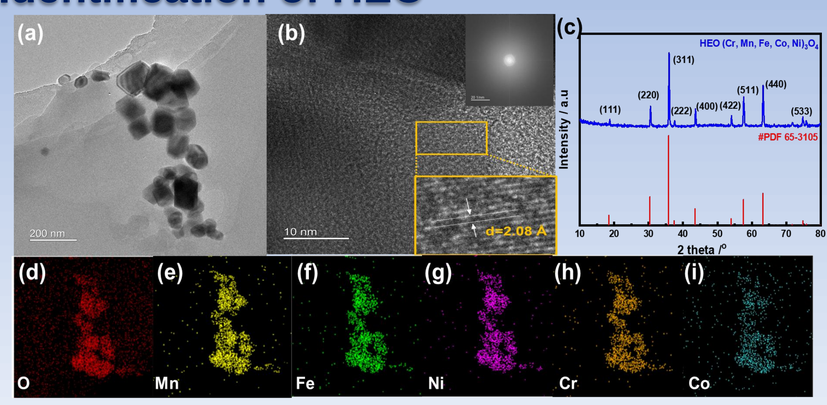
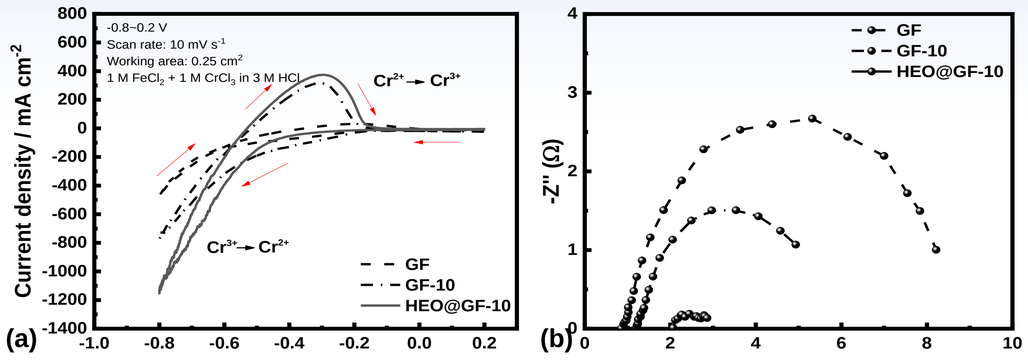


Figure 4. TEM (a), HR-TEM (b), XRD (c), and elemental mappings (d-i) of the HEO.

3 Electrochemical Testing



Name	GF	GF-10	HEO@GF-10
Ipa (mA cm^{-2})	34.6±3.6	356.9±28.3	367.2±5.1

Name	GF	GF-10	HEO@GF-10
R_{CT} (Ω cm^2)	4.0±0.8	1.0±0.1	0.3±0.1

Figure 5. (a) The CV at 10 mV s^{-1} and (b) EIS curves at a polarization potential of OCV for GF, GF-10, and HEO@GF-10 in the electrolyte solution of 1 M $FeCl_2$ + 1 M $CrCl_3$ + 3 M HCl.

4 Single-Cell Testing

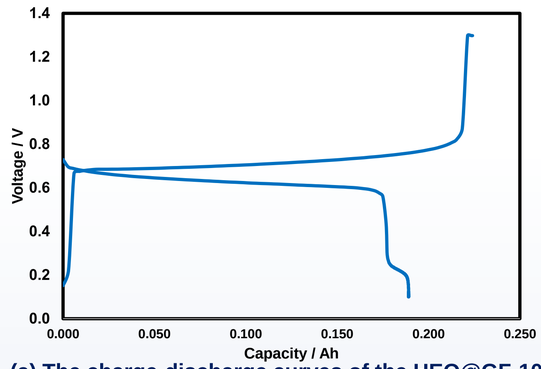


Figure 6. (a) The charge-discharge curves of the HEO@GF-10 at 40 mA/cm^2. The energy efficiency (E.E) is 70.2%.

Conclusions

In summary, a novel single-phased spinel (Cr, Mn, Fe, Co, Ni)$_3$O$_4$ high entropy oxide nanoparticles have been prepared through a CO_2 supercritical hydrothermal system pursued by post-calcination and applied as a cathode material for ICFB. Compared with GF, GF-10 electrodes, the HEO@GF-10 demonstrates the greatest electrocatalytic performance towards Cr^{3+}/Cr^{2+} redox couple. The charge/discharge tests of the ICFB single cell using the HEO catalyst exhibit good energy efficiency of 70.2% at 40 mA/cm^2.

Acknowledgements

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