Suppression of Hydrogen Evolution Reaction in Aqueous All-Iron Redox Flow Batteries

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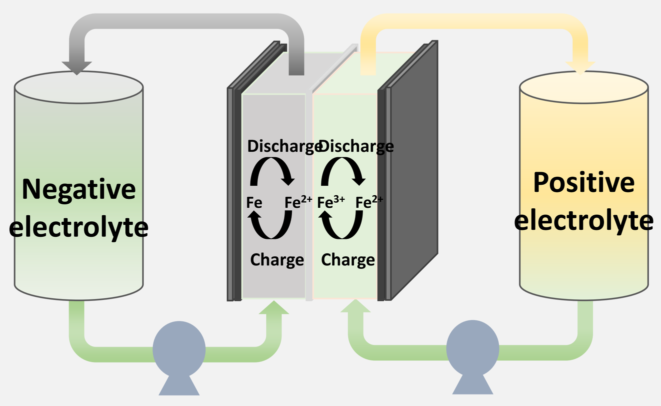
Introduction



<Fig1. All-iron Redox Flow Battery>

The all-iron redox flow battery (AIRFB) is a type of flow battery in which iron serves as the active species in both the positive and negative electrolytes. The redox couple in the positive half-cell is Fe^{2+}/Fe^{3+}, while that in the negative half-cell is Fe^{2+}/Fe^{0}

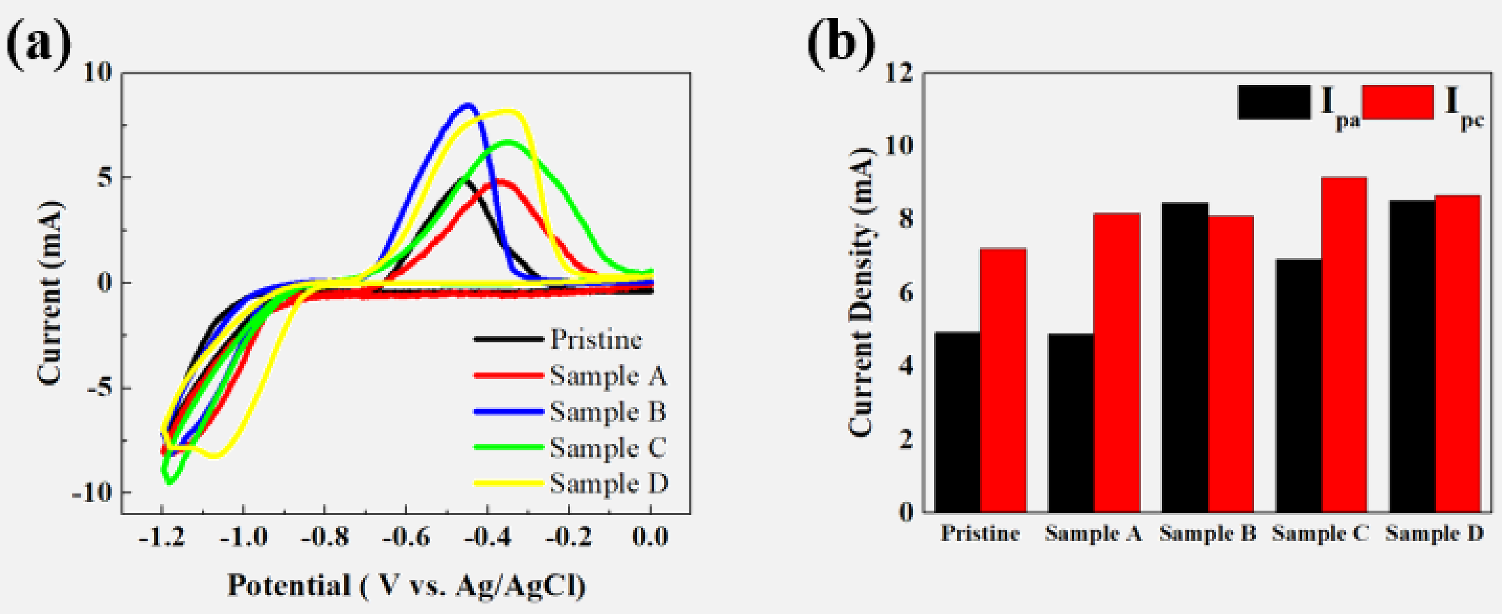
One of the major advantages of the AIRFB is its use of iron, which is an abundant and low-cost active material. Additionally, it operates over a wide temperature range, allowing for cost-effective system operation. However, a critical drawback of the AIRFB is the hydrogen evolution reaction (HER), which interferes with the pH balance of the system. This imbalance can lead to the precipitation of active materials, ultimately resulting in cell failure. To address this issue, we investigated the use of HER-suppressing additives in the negative electrolyte to enable long-term operation of the cell.

A total of four different additives were tested, each at concentrations are different. The additives were designated as **Sample A, Sample B, Sample C, and Sample D**. Electrochemical evaluation was carried out using cyclic voltammetry (CV), and full cell testing.

Results and Discussion

- **Cyclic Voltammetry (CV)**

CV measurements were carried out in the potential range of -1.2 V to 0 V with a scan rate of 20 mV/s, aiming to evaluate the effectiveness of HER suppression during the Fe^{2+}/Fe^{0} redox reaction occurring at the negative electrolyte.



<Fig2. Electrochemical performance comparison of four candidate additives: (a) CV curves and (b) I_{pa} and I_{pc} peak currents.>

The CV curves indicating that all of four candidate additives causes an increase of cathodic peak current I_{pc} as compared to the pristine. This means that all of four additives contributes to suppressing the HER, thereby enhancing the reduction kinetics of iron. Especially, sample D among them show significantly improved I_{pa} and I_{pc} which are 73% and 20% higher than those of the pristine, respectively. It also appears excellent peak current ratio (I_{pa}/I_{pc}) closest to 1 among the samples, indicating superior electrochemical reversibility.

	I_{pa} (mA)	I_{pc} (mA)	I_{pa}/I_{pc}
Pristine	4.92	7.22	0.68
Sample A	4.88	8.17	0.59
Sample B	8.47	8.11	1.04
Sample C	6.92	9.15	0.76
Sample D	8.52	8.67	0.98

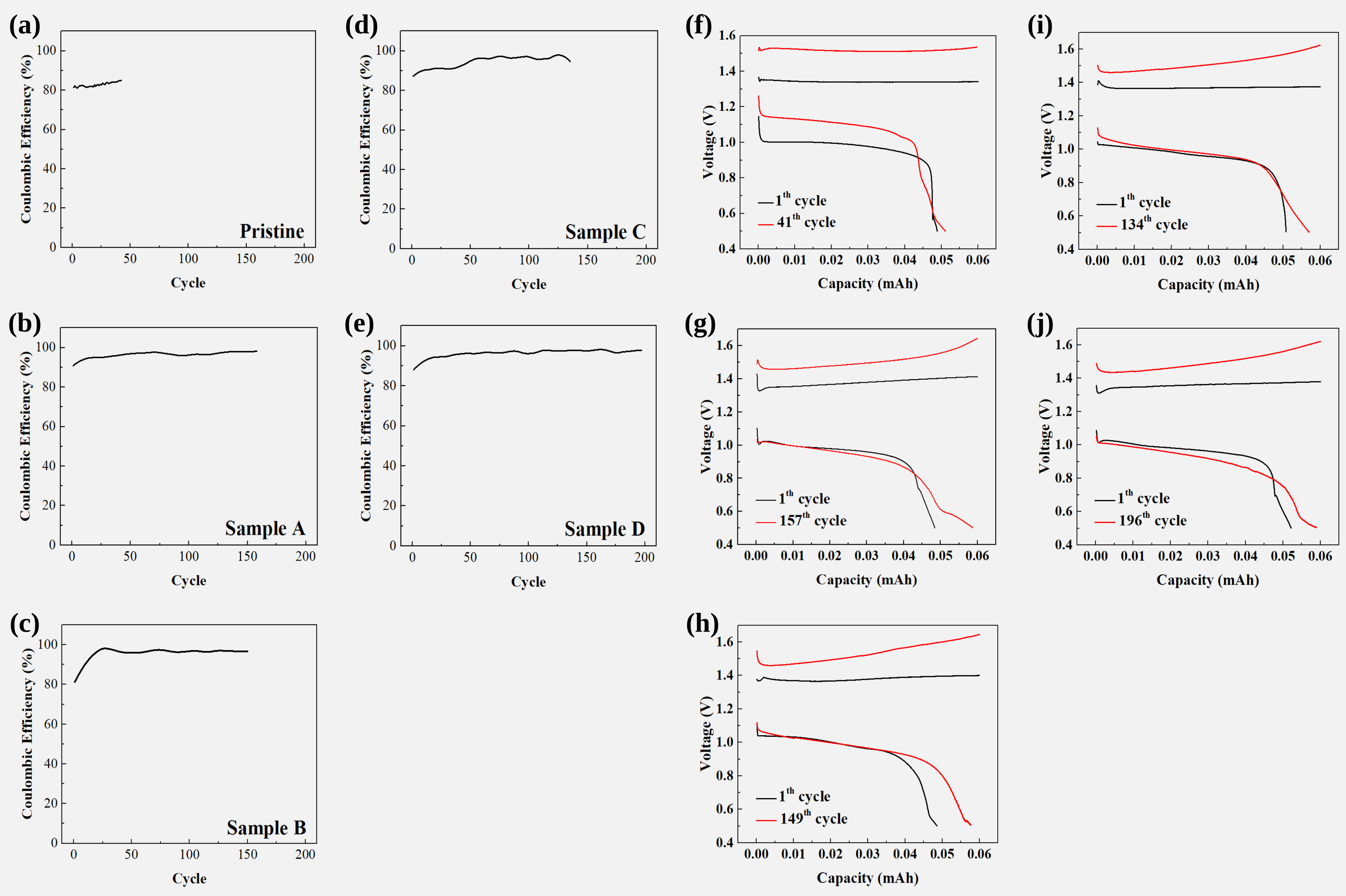
<Table1. Comparison of I_{pa} and I_{pc} peak currents between pristine and additive-containing electrolyte (Sample A-D).>

- **Full-cell test**

✓ Current Density : 20 mA/cm² (constant current)

✓ Charge Process : 30 min

✓ Discharge Process : 0.5 V voltage cutoff



<Fig3. (a-e) Coulombic efficiency comparison for pristine cell and sample A-D, (f-j) Voltage-capacity profiles comparing the 1st (black) and final (red) cycles for pristine and sample A-D.>

	Cycle life	CE over the full cycle life (%)
Pristine	41	82.84
Sample A	157	94.44
Sample B	149	95.84
Sample C	134	94.53
Sample D	196	96.37

<Table2. Cycle life and average coulombic efficiency (CE) over the full cycle life for the pristine cell and cells A-D.>

Conclusion

Enhanced reduction currents in CV indicated successful suppression of HER, allowing the iron redox reaction to proceed more efficiently. The full-cell cycling tests reinforce this finding, with additive-containing cells operating 3 to 5 times longer than the pristine cell and showing over 12% higher CE in most cases. These results confirm that the selected additives not only enhance electrochemical activity in half-cell conditions but also significantly contribute to the durability and stability of full-cell operation. The ability to maintain stable performance over extended cycling demonstrates the effectiveness of HER suppression in prolonging cell life.

Future work will focus on clarifying the interaction between additives and electrode surfaces using in-situ or spectroscopic techniques. In addition, the scalability and performance of these additives under practical operating conditions will be evaluated.

Acknowledgements

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