IRON PREPLATING AS A METHOD OF INCREASING COULOMBICEFFICIENCY OF AN ALL-IRON REDOX FLOW BATTERY

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In recent years, there has been a substantial increase in the installation of wind and solar power plants, driven by political and social demands for a transition to renewable energy. Despite this progress, the energy sector still contributes 55 % of total carbon dioxide emissions, necessitating initiatives to reduce both this percentage and the absolute amount of carbon dioxide produced [1,2]. The increasing proportion of unpredictable renewable energy generation requires a corresponding increase in flexible electricity generation to maintain balance in the power grid. Consequently, there is a need to develop tools for the long-term storage of "green" electricity, which would enhance the predictability of renewable energy production and provide flexible generation capacity [3]. This development would enable society to expand the number of solar and wind power plants without the need for parallel expansion of coal-based generation.

Promising candidates for medium- (hours and days) and long-term (weeks and months) storage technologies can be: hydropower plants; hydrogen production and transformation technologies; mechanical (gravity) storage technologies; compressed air storage technology; and redox flow batteries.

Redox flow batteries offer relatively high efficiency and are not affected by landscape variations, making them advantageous compared to other technologies. Among the different types of flow batteries, those based on the following chemical element pairs have been the most extensively researched and developed [4–8]: V/V; Zn/O_2; Zn/Br_2; H_2/Br_2; Fe/Cr; Fe/Fe; Zn/Ce.

Considering the availability and simplicity of iron extraction, and the availability of graphite and other materials necessary for large-scale production in Ukraine, the research and development of industrial energy storage systems based on Fe/Fe^{3+} redox couple is quite promising.

At the positive electrode ferrous ions are oxidized to ferric ions; at the negative electrode ferrous ions are reduced and metallic iron is deposited. During battery discharge these processes occur in the opposite way: metallic iron is oxidized and dissolves in the electrolyte at the negative electrode while ferric ions are reduced to ferrous ions at the positive electrode:

$$\text{Positive electrode: } Fe^{2+} \rightarrow Fe^{3+} + e,\ E^{+}_{0} = 0{,}77\ V$$

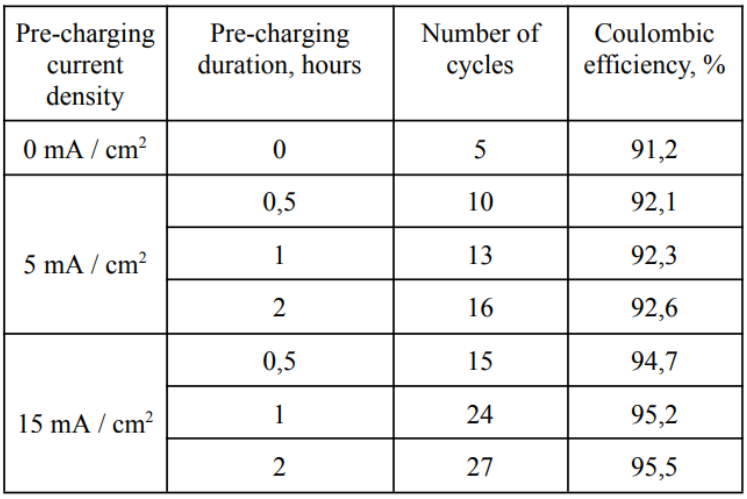
$$\text{Negative electrode: } Fe^{2+} + e \rightarrow Fe_{S},\ E^{-}_{0} = -0{,}44\ V$$

$$\text{Overall reaction: } 3Fe^{2+} \rightarrow 2Fe^{3+}\ Fe_{S},\ \Delta E^{0} = 1{,}21\ V$$

During the charging process, iron deposition on porous graphite primarily results in the formation of large, non-uniform crystals. These irregular crystals facilitate the hydrogen evolution reaction on their surfaces. To mitigate the rate of hydrogen evolution, we propose an iron preplating stage, which involves a pre-charging deposition process at a lower current density to form smaller, more uniform crystals. Implementing this preplating stage enhances the subsequent charge-discharge cycles, leading to higher coulombic efficiency.

The summarized research results are described in the table 1.

Table 1 – Coulombic efficiency for an all-iron redox flow battery charge-discharge cycles



Pre-charging current density	Pre-charging duration, hours	Number of cycles	Coulombic efficiency, %
0 mA / cm^2	0	5	91,2
5 mA / cm^2	0,5	10	92,1
	1	13	92,3
	2	16	92,6
15 mA / cm^2	0,5	15	94,7
	1	24	95,2
	2	27	95,5

When a low pre-charging current density of 5 mA/cm² was applied, the coulombic efficiency showed a progressive improvement with increased pre-charging duration. Specifically:

- 0.5-hour pre-charging duration resulted in a 0.9% increase in efficiency (92,1%).
- Extending the duration to 1 hour further improved the efficiency to92,3 %.
- 2-hour pre-charging duration achieved the highest efficiency in thiscategory, at 92,6 %.

At a higher pre-charging current density of 15 mA/cm², there was a significant improvement in coulombic efficiency. The efficiency gains were more pronounced compared to the lower current density

- 0,5-hour pre-charging duration resulted in an efficiency of 94,7 %, anotable increase from the baseline.
- Increasing the pre-charging duration to 1 hour further improved theefficiency to 95,2 %.
- 2-hour pre-charging duration resulted in the highest observed efficiency of 95,5 %.

The data demonstrates that implementing a pre-charging stage with iron deposition at a lower current density can substantially enhance the coulombic efficiency of all-iron redox flow batteries. The improvement is attributed to the formation of smaller, more uniform iron crystals during the pre-charging process, which reduces the surface area available for hydrogen evolution reactions.

- At 5 mA/cm²: Even a low pre-charging current density significantly improves efficiency, with longer durations leading to incremental gains.
- At 15 mA/cm²: A moderate pre-charging current density yields even greater improvements, with efficiencies exceeding 94 % afte

- 0,5 hours and reaching up to 95,5 % with longer pre-charging durations.

The introduction of a pre-charging stage at appropriate current densities effectively enhances the performance of all-iron redox flow batteries. The data suggests that pre-charging at 15 mA/cm² for 2 hours provides the highest efficiency, making it a promising approach for optimizing the charge-discharge cycles in these batteries. Further research could explore the effects of varying current densities and durations to refine this pre-charging strategy and maximizebattery performance.

References

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[3] D. Gielen et al., Energy Strategy Reviews, 24, 38 (2019). Figure 10. (a) Total amount of metal plated (in units of charge) obtained by integrating anodic sweep depicted in Fig. 9 between −0.70 and +0.35 V, before the onset of Fe2+ oxidation. (b) Influence of supporting cation on onset potentials and overpotential difference in the linear sweep voltammogram. Figure 11. Partial current density of HER and Fe deposition (a), and the corresponding coulombic efficiency (b). Data obtained by quantitative anodic stripping voltammetry method on a Au RDE rotating at 2000 rpm, with plating time of 30 s, in electrolyte of 2.0 M XCl, 1.5 M FeCl2, pH = 2.0. Each data point is the average of four scans. Journal of The Electrochemical Society, 2021 168 040529

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