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RARE METALS

HIGHLIGHT

Nuclei-rich galvanizing strategy for suppressing zinc dendrite growth

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The uncontrolled growth of zinc dendrites on zinc anode hinders the application of zinc ion batteries. To solve this problem, Lu's group proposed a nuclei-rich galvanizing strategy for suppressing the zinc dendrite growth. This allows the nuclei-rich zinc electrode to cycle steadily for 1200 h and have a high Coulombic efficiency of 99.7% at 15 mA·cm^{-2} with a deposited amount of 10 mAh·cm^{-2}. Moreover, the Zn-MnO_2 battery with a low N/P ratio of 1.9 exhibited sustained cycling life.

Zinc ion batteries (ZIBs) are believed to be a promising candidate to replace traditional lithium-ion batteries in some applied fields due to their high safety, large specific capacity and low cost [1–3]. However, the limited cycling life and low Coulombic efficiency hinder the use of Zn metal, which is associated with the undesirable growth of Zn dendrites during cycling process [4, 5]. Theoretically, the essence of Zn dendrite growth is attributed to the non-uniform nucleation driven by the uneven distribution of Zn^{2+} concentration [6–9]. In order to inhibit Zn dendrite growth and side reactions on Zn anode, various strategies have been presented, e.g., structural construction of Zn electrodes, surface passivation, separator modification, electrolyte optimization, etc. [10–13]. For ZIBs, the uniform Zn deposition during the galvanizing process is crucial, but remains challenging.

Lu's group recently reported a nuclei-rich galvanizing strategy for constructing a nucleation interface with high ionic conductivity and nucleation catalytic activity by directly contacting hydroxyapatite surface with Zn [14], which could totally change Zn electroplating way through consistent production of numerous crystal nuclei, so that dense Zn crystals with small radii and high uniformity can form. In traditional means (Fig. 1a), the tip of the non-smooth Zn surface would increase the local current density and generate a high-intensity uneven electric field during battery cycling process, so that a large number of free Zn^{2+} would be adsorbed and concentrated on these tips for preferential deposition. In continuous cycling process, Zn^{2+} tended to grow on the existing crystal nuclei to form Zn dendrites gradually. In nuclei-rich galvanizing process (Fig. 1b), ZIBs with incubating interface had a high rate of progressive nucleation. Unlike the common progressive nucleation, the amount of nucleation in initial charge/discharge process was five times higher than that of the ordinary battery. Thus, the number of nucleation would increase sharply with the cycling process, while the radius of the nucleus decreases. Therefore, the nuclei incubating interface could exhibit more uniform charge distribution for uniform and dense Zn deposition.

Compared with traditional Zn|Zn cell in Fig. 1c, Zn|Zn cell was greatly improved after introducing nucleus-rich structure. After cycled at 1 mA·cm^{-2} after 252 h, the voltage of traditional Zn|Zn cell suddenly dropped due to the battery short circuit. When 15 mA·cm^{-2} was applied, the cycling performance was obviously enhanced (Fig. 1d). The traditional Zn|Zn cell cycled for below 100 h, while the nuclei-rich Zn|Zn cell exhibited stable cycling over 1200 h. Moreover, the nuclei-rich Zn||MnO_2 battery in Fig. 1e kept an average capacity of 1.4 mAh·cm^{-2} after 3000 cycles with the Coulomb efficiency of 99.97% at 10C, while traditional Zn||MnO_2 battery just ran for less than 400 cycles. The pouch cells constructed with nuclei-rich Zn electrode in Fig. 1f could stably cycle for more

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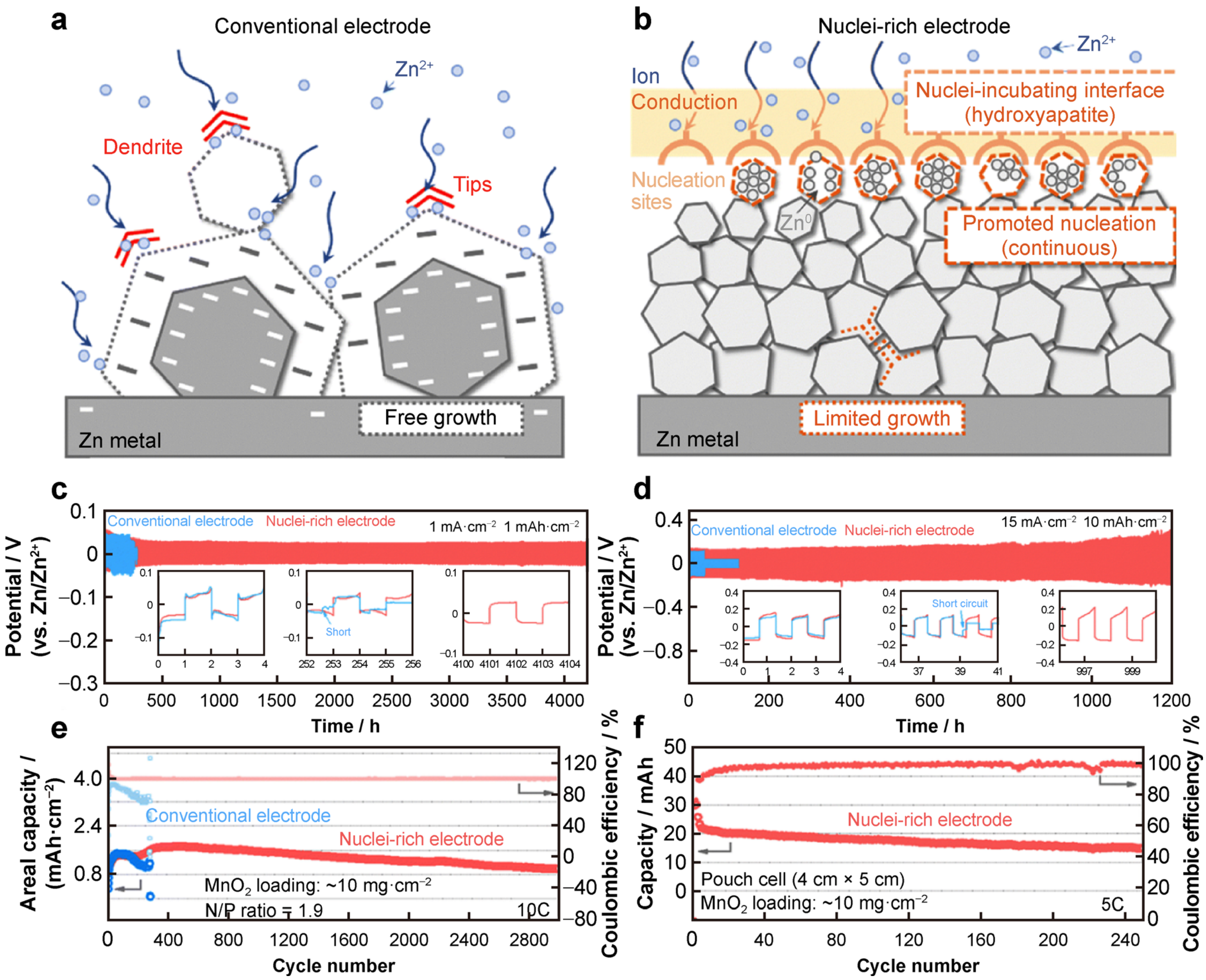

Fig. 1 Zn plating: **a** conventional strategy and **b** nuclei-rich Zn strategy; **c** cycling performance of nuclei-rich Zn|Zn cell cycled at 1 mA·cm^{-2} with a deposit amount of 1 mAh·cm^{-2}; **d** cycling performance of nuclei-rich Zn|Zn cell cycled at 15 mA·cm^{-2} with a deposit amount of 10 mAh·cm^{-2}; **e** compared cycling performance of bare Zn||MnO_2 batteries cycled at 10C; **f** compared cycling performance of pouch cells cycled at 5C. Reproduced with permission from Ref. [14]. Copyright 2023, RSC Publishing

than 250 times at 5C, indicating potential for commercialization.

In conclusion, Lu's group proposed the nuclei-rich galvanizing strategy which can effectively inhibit Zn dendrite growth. The nuclei-rich Zn anode could significantly inhibit the dendrite growth with a Coulomb efficiency of 99.7%. Such Zn anode achieved the long cycling with low negative/positive ratio of the whole battery and led to pouch cells with good performance. This work not only demonstrates a novel idea to improve the Zn plating/stripping reversibility, but also provides important guidance for other metal anodes (e.g., lithium, sodium, and magnesium).

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Declarations

Conflict of interests The authors declare that they have no conflict of interest.

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