The corrosion behavior of nickel cathodes in electrolytic water used for hydrogen evolution

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Abstract In this study, we examined the cathodic corrosion processes and the associated mechanisms of hydrogen evolution reaction (HER) performance deterioration on nickel (Ni) cathode electrodes. The experiments were conducted in an 85 wt.% KOH solution at 160 °C, covering a range of current densities.

It was found that corrosion initiated at an onset potential of –1.7 V vs. Pt. At lower current densities (2-20 mA cm^{-2}), where the potential was more positive than this threshold, no significant corrosion was observed. In contrast, at higher current densities (200-500 mA cm^{-2}), the potential dropped negatively at the onset, leading to severe corrosion with rates as high as 125.49×10^{-3} mm y^{-1}. Corrosion manifested as pitting, which preferentially initiated at sites of high surface activity, such as defects and scratches, and then propagated laterally and vertically across the Ni surface. This cathodic corrosion led to significant surface recrystallization, with the polarization process promoting the dissolution of high-energy (200) and (220) facets, while the low-energy (111) facets were favored for nucleation and redeposition of Ni atoms. Cathodic corrosion induced an increase in surface roughness and a subsequent decline in HER performance. This increase in roughness, not only expanded the specific surface area of the Ni electrode but also reduced the number of genuine active sites available for hydrogen evolution.

Our findings underscored the significant influence of cathodic corrosion on the endurance and efficacy of Ni-based HER electrodes, identifying the anisotropic orientation of Ni grains, induced by cathodic corrosion, as the principal driver of performance degradation.

Keywords Nickel cathode, Cathodic corrosion, Hydrogen evolution, Electrochemistry