

Supporting Information

Highly Efficient Water Electrolysis Using NaOH–KOH Hydrate Melt

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Equilibrium potentials of Pd–H electrode and OER vs. RHE

The equation of the equilibrium potential of Pd–H electrode vs. RHE is as follows:

$$E_{\text{Pd-H vs. RHE}} = \frac{RT}{2F} \ln \left(\frac{P}{P^0} \right)$$

where P is the equilibrium hydrogen pressure in the two-phase coexistence region of Pd–H, P^0 is the standard pressure (1.013×10^5 Pa), T is the temperature, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and F is the Faraday constant ($9.6485 \times 10^4 \text{ C mol}^{-1}$). The values of $\ln \left(\frac{P}{P^0} \right)$ were calculated based on the relationship between P and temperature.²⁸ P from the literature²⁸ at each temperature is as follows: 9.629×10^{-3} Pa (80 °C), 2.069×10^{-4} Pa (100 °C), 4.149×10^{-4} Pa (120 °C), 1.035×10^{-5} Pa (150 °C), 2.207×10^{-5} Pa (180 °C), and 3.355×10^{-5} Pa (200 °C).

The equation of the equilibrium potential of OER vs. RHE is as follows:

$$E_{\text{OER vs. RHE}} = E^0 - \frac{RT}{2F} \ln \frac{a_{\text{H}_2\text{O}}}{(P_{\text{O}_2}/P^0)^{1/2} \cdot (P_{\text{H}_2}/P^0)}$$

where E^0 is the standard theoretical decomposition voltage, $a_{\text{H}_2\text{O}}$ is the activity of H_2O in the electrolyte, P_{O_2} is the partial pressure of evolved O_2 at the electrode surface, and P_{H_2} is the partial pressure of evolved H_2 at the electrode surface. The equilibrium potentials in Table 1 (b) are potentials when $\frac{a_{\text{H}_2\text{O}}}{(P_{\text{O}_2}/P^0)^{1/2} \cdot (P_{\text{H}_2}/P^0)} = 1$. E^0 at each temperature was calculated using the following equation:

$$E^0 = -\frac{\Delta G^0}{2F}$$

where ΔG^0 is the standard Gibbs free energy for the formation of H_2O (g).

Reference

28 F. D. Manchester, A. San-Martin, and J. M. Pitre, *J. Phase Equilib.*, **15**, 62 (1994).

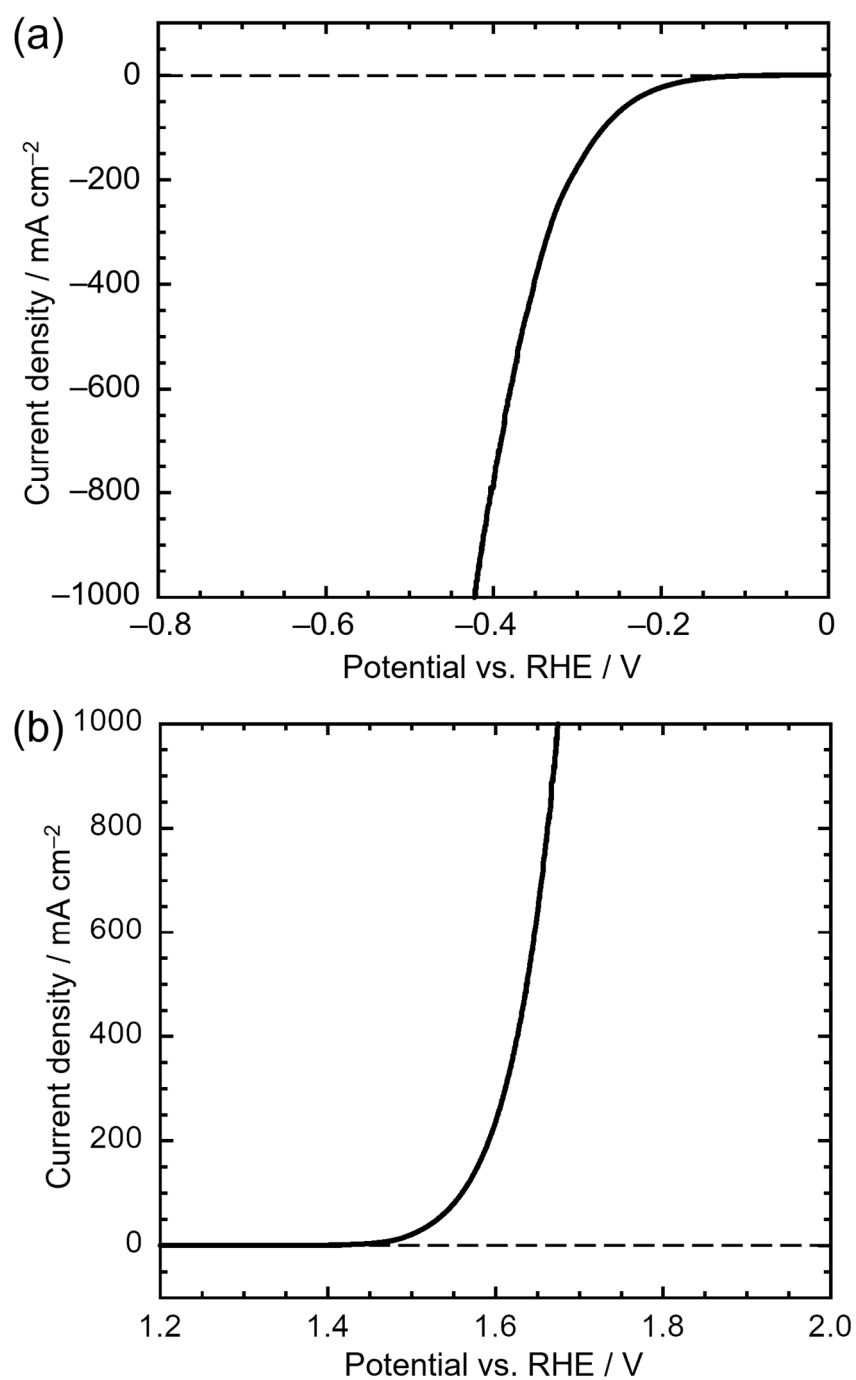


Figure S1. Linear sweep voltammograms for (a) HER and (b) OER in 85 wt% KOH hydrate melt at 150 °C. Scan rate: 10 mV s^{-1} .