Supporting Information For:

Effects of Dissolved 3d-block Metal Ions on PEM Water Electrolysis Performance

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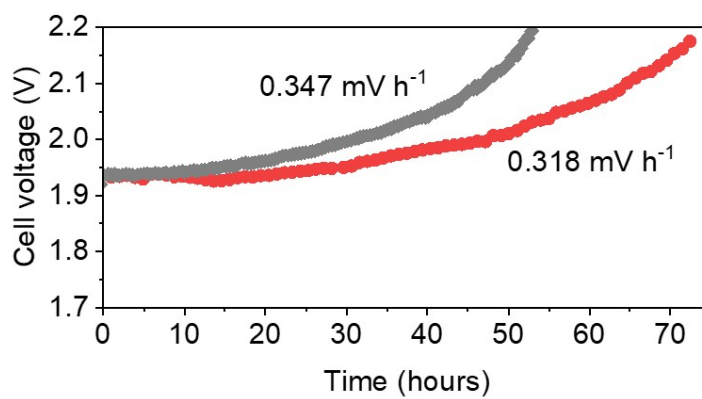
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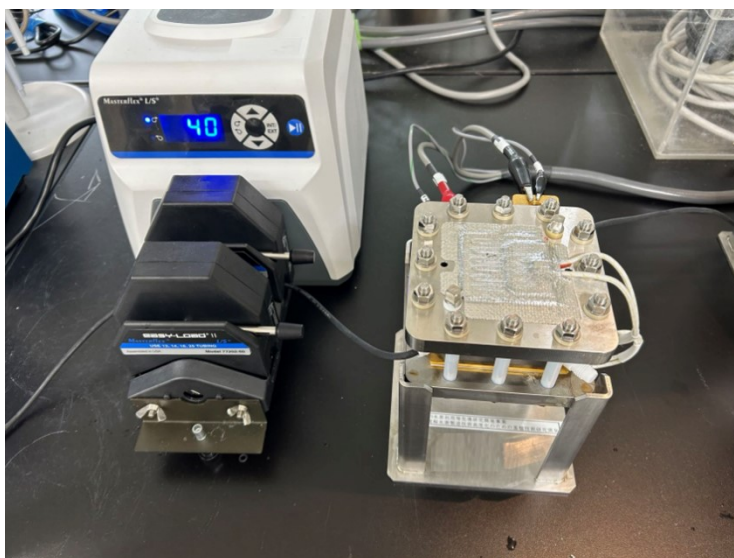
Fig. S1. Set-up of the PEM electrolyzer used in this study.
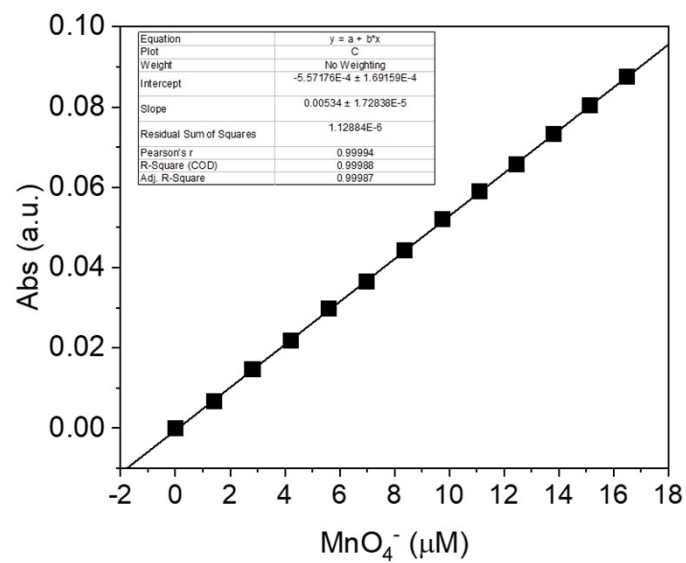
Fig. S2. Calibration curve of absorbance versus MnO_4^- concentration in 1 M H_2SO_4. The inset table shows the parameters used for the linear fit.

Fig. S3. Long-term stability test of PEM water electrolysis at 1 A cm^{-2} in the presence of MnO_4^- (grey line) and in the absence of MnO_4^- (red line). γ-MnO_2 was used as the anode catalyst. The temperature is 80 °C. The deviation in the degradation rate is attributable to the decomposition of MnO_4^- into MnO_2 accompanied by oxygen release.
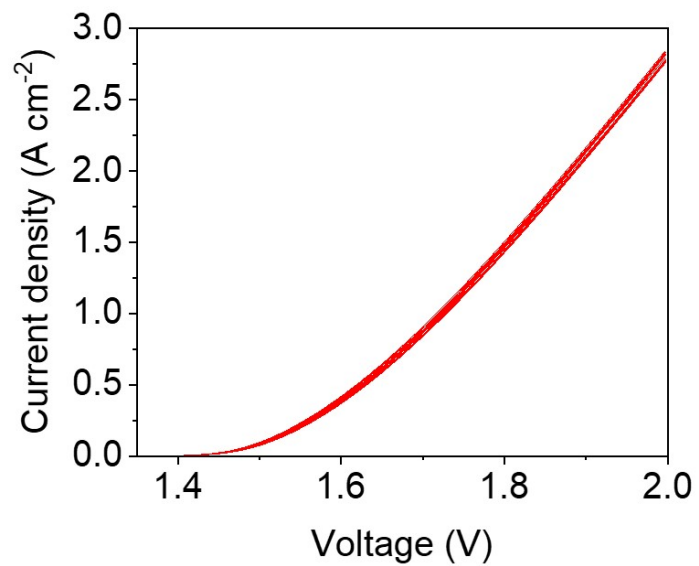
Fig. S4. 20 Linear sweep voltammetry scans performed during PEM water electrolysis using a 0.08 mg/cm² Ir catalyst on the anode side.
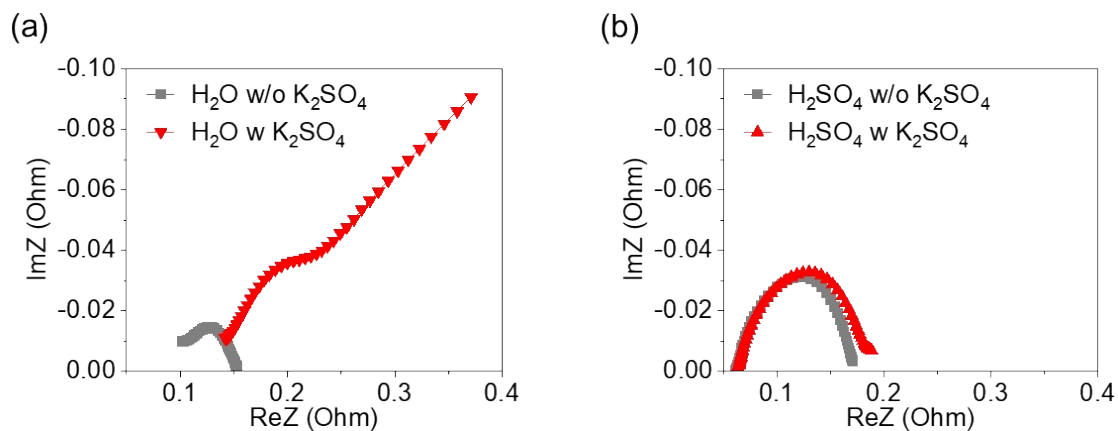
**Fig. S5**. (a) Electrochemical impedance spectra at 1.8 V measured in the presence and absence of K_2SO_4 in PEM water electrolysis. (b) Electrochemical impedance spectra at 1.8 V measured in the presence and absence of K_2SO_4 in 0.05 M H_2SO_4 in PEM water electrolysis.
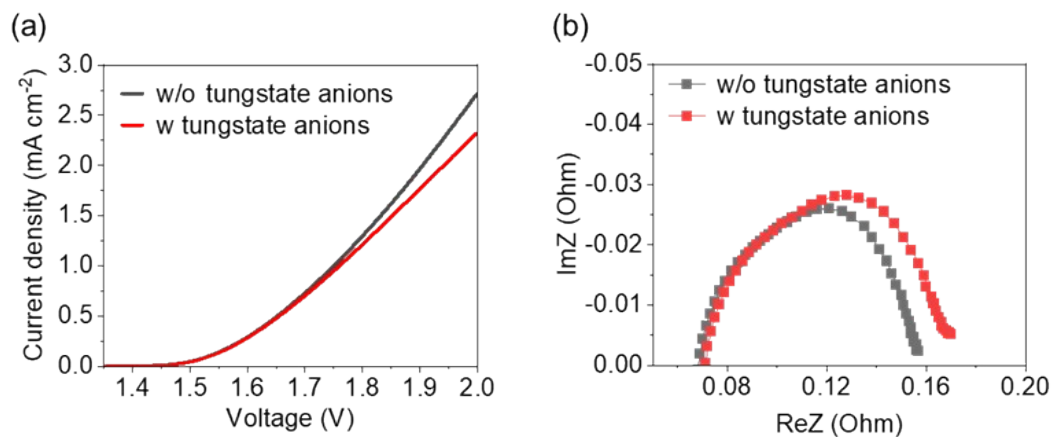
Fig. S6. (a) Linear sweep voltammetry scans (LSV) were performed during PEM water electrolysis with and without a direct feed of Na_2WO_4. (b) Electrochemical impedance spectra at 1.8 V were measured in the presence and absence of Na_2WO_4 over a frequency range of 100 kHz to 1 Hz.
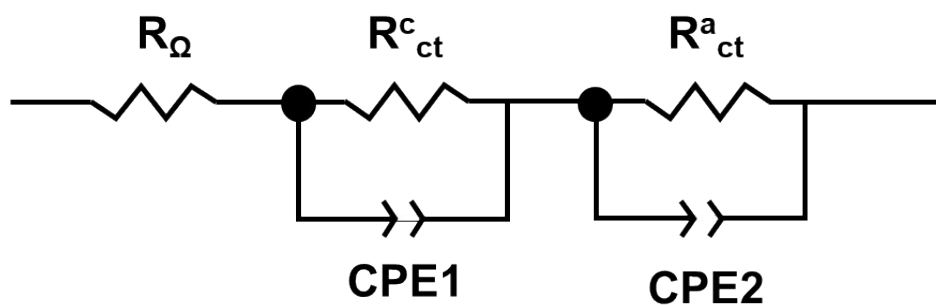
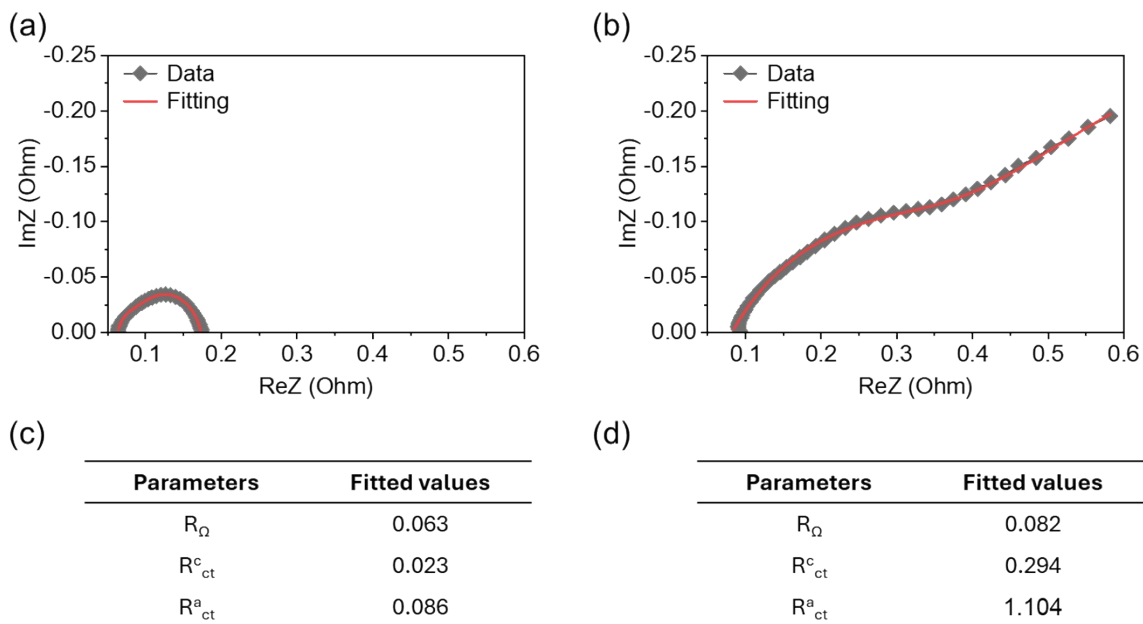**Fig. S7**. Diagram of the electrical circuits used to model impedance spectra. An Ohmic resistor (R_Ω) was connected in series with two parallel components, which consisted of a resistor (R^a_{ct} or R^c_{ct}) and a constant phase element (CPE).

(a)

(b)

(c)

Parameters	Fitted values
R_Ω	0.062
R^c_{ct}	0.024
R^a_{ct}	0.065

(d)

Parameters	Fitted values
R_Ω	0.061
R^c_{ct}	0.024
R^a_{ct}	0.079
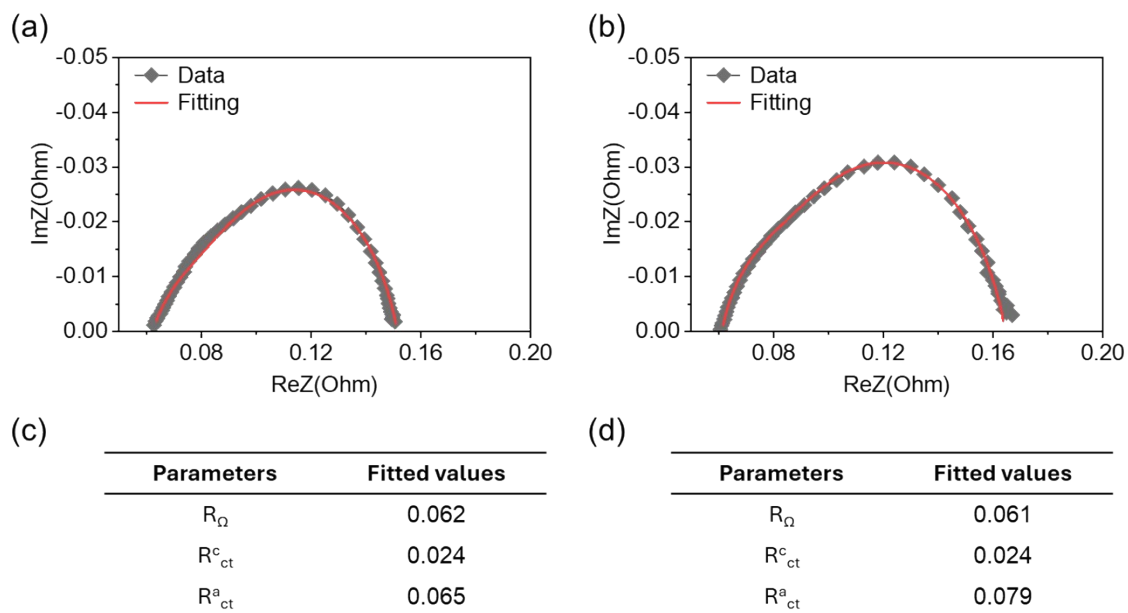
Fig. S8. Impedance spectra measured at 1.8 V during PEM electrolysis conducted with a feed solution of 0.05 M H_2SO_4 (a) or with 1 mM $KMnO_4$ in 0.05 M H_2SO_4 (b). Dotted lines represent the raw data and solid curves show the fitted results. The fitting parameters are displayed in (c) and (d), respectively.

(a)

(b)

(c)

Parameters	Fitted values
R_Ω	0.063
R^c_{ct}	0.023
R^a_{ct}	0.086

(d)

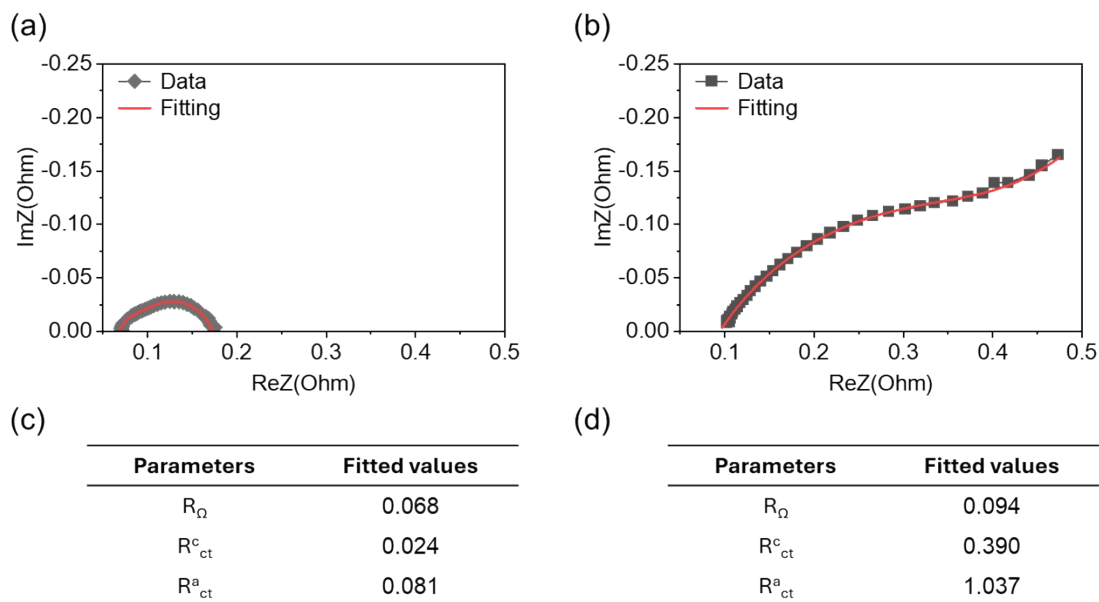| Parameters	Fitted values
R_Ω	0.082
R^c_{ct}	0.294
R^a_{ct}	1.104

Fig. S9. Impedance spectra measured at 1.8 V during PEM electrolysis conducted with a feed solution of 0.05 M H_2SO_4 (a) or with 1 mM Ni^{2+} in 0.05 M H_2SO_4 (b). Dotted lines represent the raw data and solid curves show the fitted results. The fitting parameters are displayed in (c) and (d), respectively.

(a)

(b)

(c)

Parameters	Fitted values
R_Ω	0.068
R^c_{ct}	0.024
R^a_{ct}	0.081

(d)

Parameters	Fitted values
R_Ω	0.094
R^c_{ct}	0.390
R^a_{ct}	1.037

Fig. S10. Impedance spectra measured at 1.8 V during PEM electrolysis conducted with a feed solution 0.05 M H_2SO_4 (a) or with 1 mM Co^{2+} in 0.05 M H_2SO_4 (b). Dotted lines represent the raw data and solid curves show the fitted results. The fitting parameters are displayed in (c) and (d), respectively.