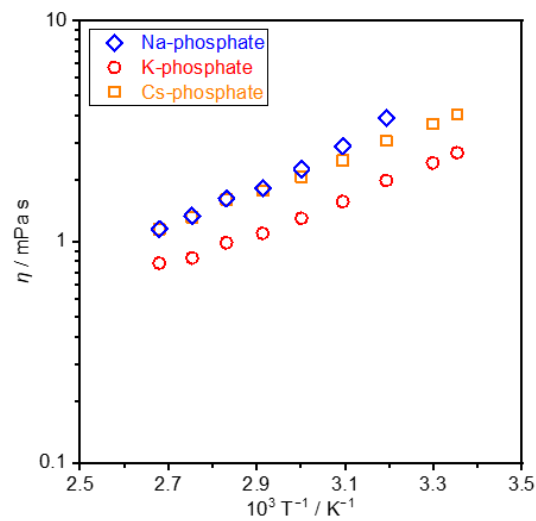


# ChemSusChem

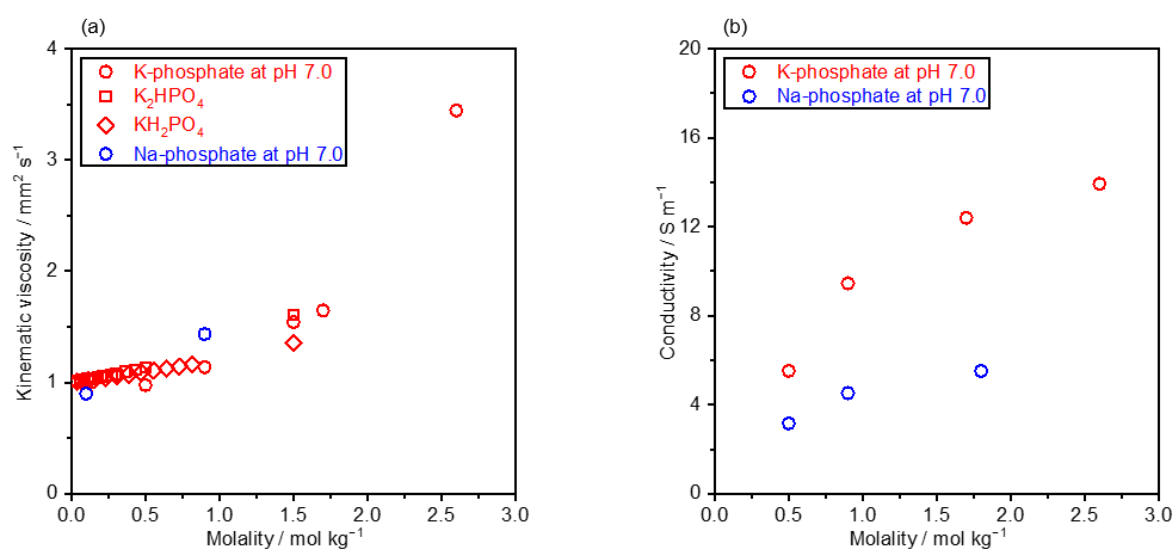
## Supporting Information

### **Water Electrolysis in Saturated Phosphate Buffer at Neutral pH**

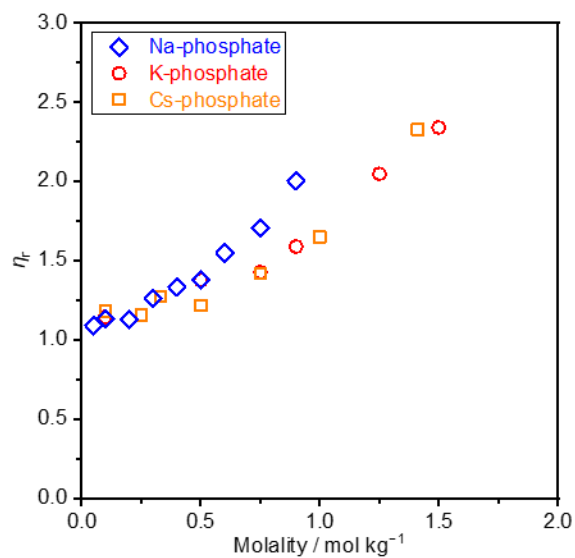
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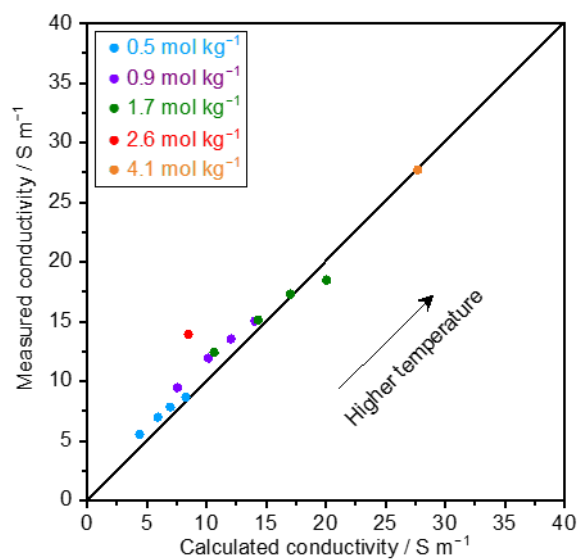
**Figure S1.** The Arrhenius type plot of viscosity in 2.0 mol kg<sup>-1</sup> *M*-phosphate (*M*=Na, K and Cs) solutions. Viscosity of the Na-, K-, and Cs-phosphate solutions was measured using a viscometer, and is plotted as a function of the reciprocal of the temperature. pH levels of the phosphate solutions were adjusted to 7.0 at 25 °C prior to the measurements.



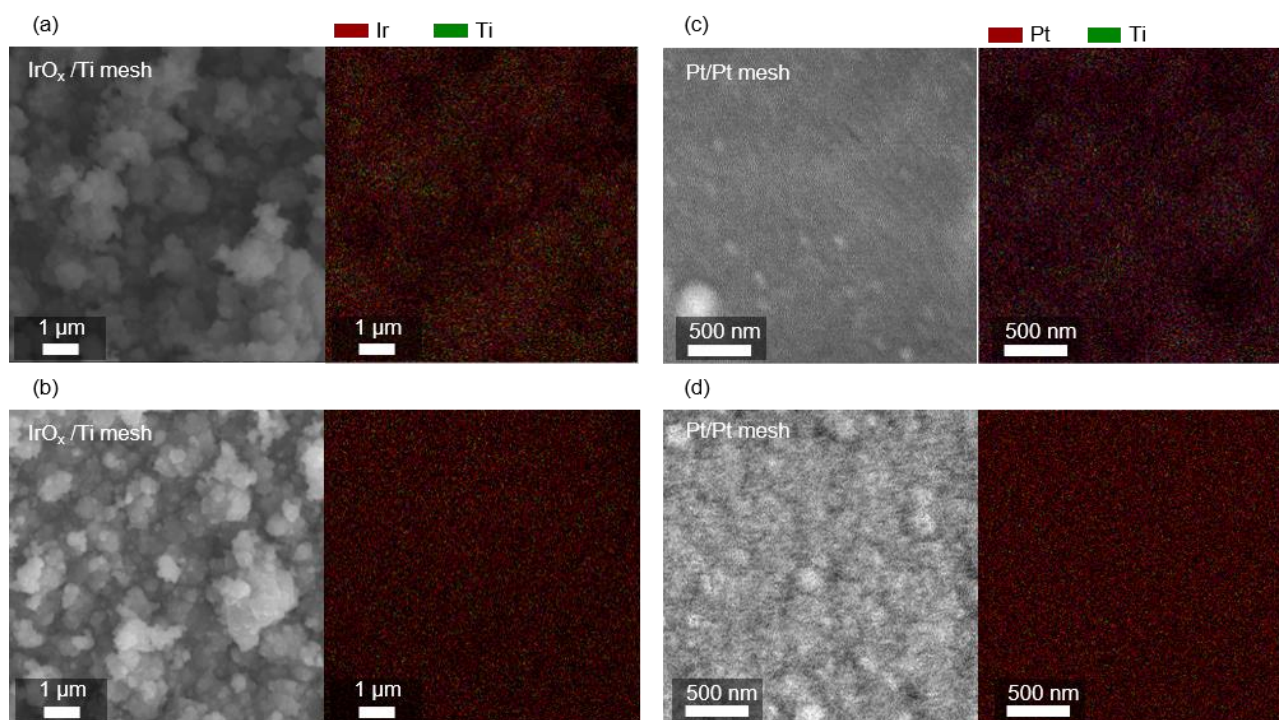
**Figure S2.** Physicochemical properties of K- and Na-phosphate as a function of concentration. (a) Viscosity of the K- and Na-phosphate solutions was measured at 25 °C using a viscometer. Viscosity of  $\text{KH}_2\text{PO}_4$  and  $\text{K}_2\text{HPO}_4$  solutions were adopted from the literature.<sup>[S1]</sup> (b) Conductivity of the K-phosphate solutions at 25 °C and Na-phosphate solutions at 30 °C were plotted as a function of molality and assessed by impedance conducted in the 2-electrode system using two Pt wires while keeping the distance between Pt wires at 2.0 cm (cell constant,  $K_{\text{cell}} = 0.6 \text{ cm}^{-1}$ ). In both panels, the pH levels of solutions were adjusted to 7.0 at 25 °C prior to the measurements.



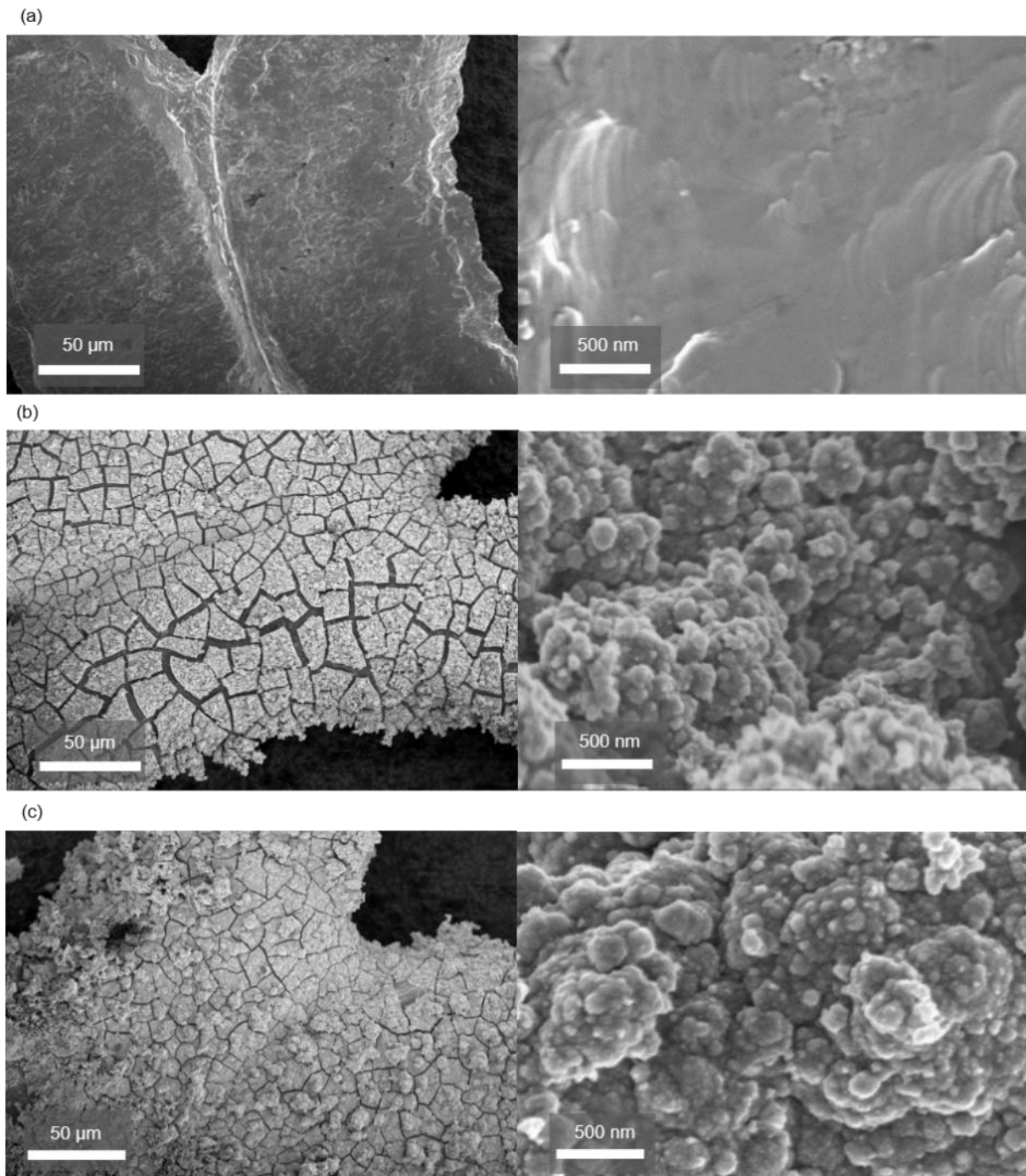
**Figure S3.** The parameter  $\eta_r (= \eta / \eta_0)$  as a function of molality of Na-, K-, and Cs-phosphate solutions at 25 °C. Viscosity of the Na-, K-, and Cs-phosphate solutions was measured at 25 °C using a viscometer. pH levels of the phosphate solutions were adjusted to 7.0 at 25 °C prior to the measurements.



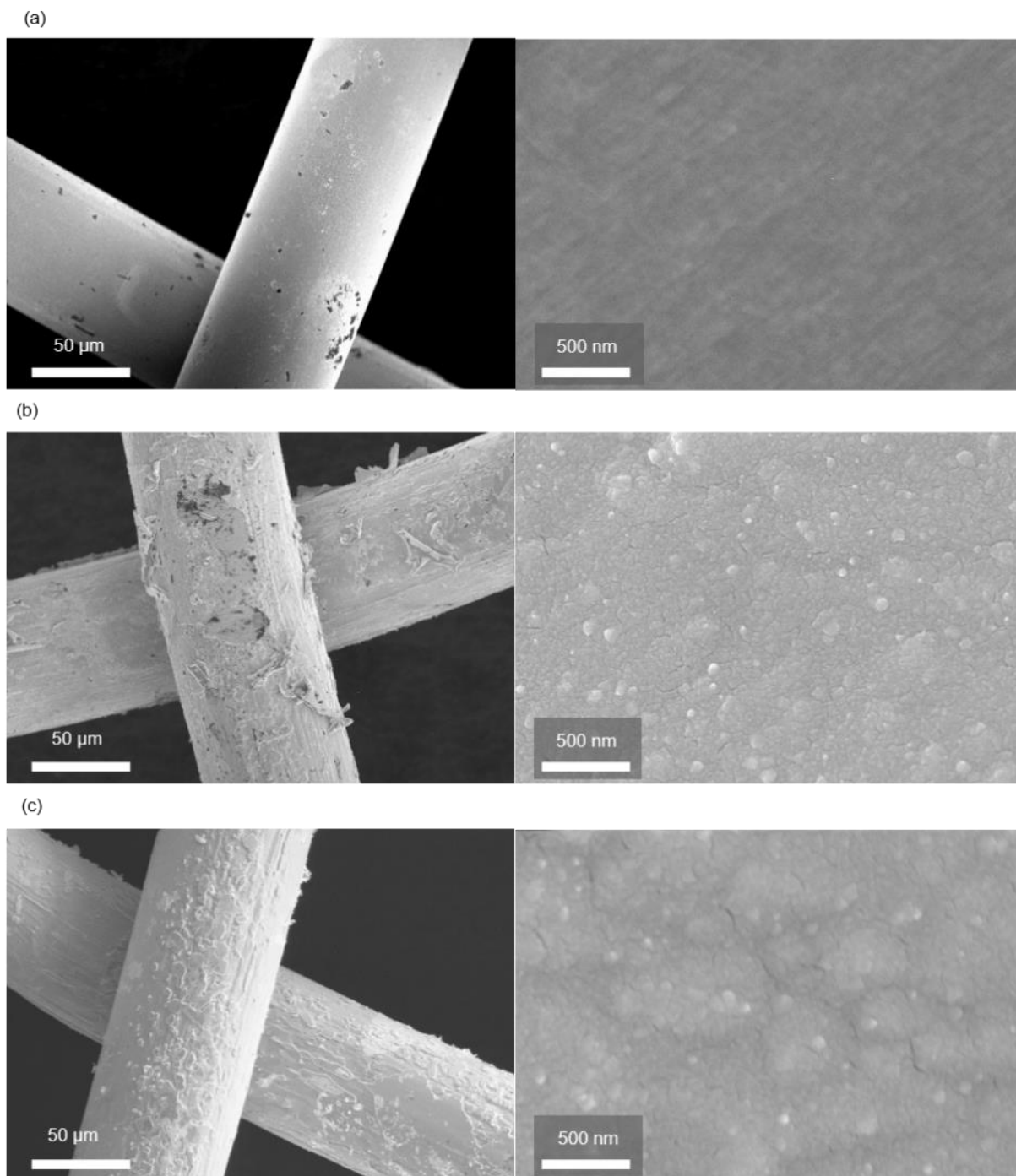
**Figure S4.** Comparison of experimentally obtained and calculated conductivity. The experimentally observed conductivity was compared with the value derived from calculations for various K-phosphate solutions at molalities of 0.5, 0.9, and 1.7 mol kg<sup>-1</sup> at varying temperatures of 25, 40, 50 and 60 °C as well as 2.6 mol kg<sup>-1</sup> and 4.1 mol kg<sup>-1</sup> K-phosphate at temperatures of 25 and 100 °C. Conductivity was experimentally measured by impedance spectroscopy, which was conducted in the two-electrode system using two Pt wires while keeping the distance between Pt wires at 2.0 cm (cell constant,  $K_{\text{cell}} = 0.6 \text{ cm}^{-1}$ ). The calculated conductivity was obtained by using Stokes-Einstein equation.



**Figure S5.** Surface morphology of model electrodes. Scanning electron microscopy (SEM) images of (a,b) IrO<sub>x</sub>/Ti mesh and (c,d) Pt/Pt mesh. The panels (a) and (b) show the as-prepared electrodes while panels (c) and (d) show the pot-reaction ones. The corresponding energy dispersive x-ray spectroscopy (EDS) mapping is displayed next to each SEM image.

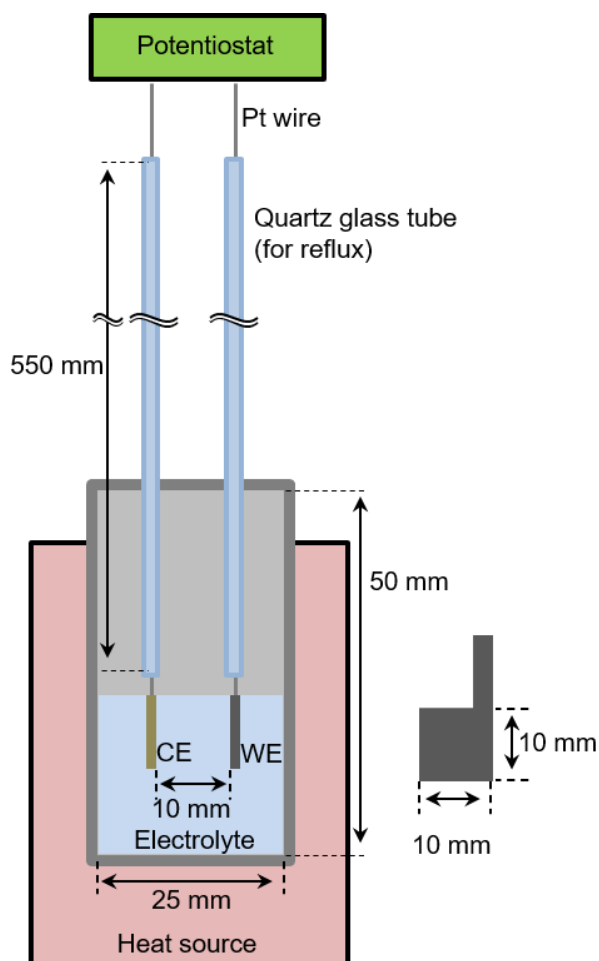


**Figure S6.** Surface morphology of IrO<sub>x</sub>/Ti mesh. SEM images of (a) bare Ti mesh, (b) fresh IrO<sub>x</sub>/Ti mesh, and (c) used IrO<sub>x</sub>/Ti mesh electrodes. All figures on the left were taken in high resolution, and the corresponding images at lower magnification are shown on the right.

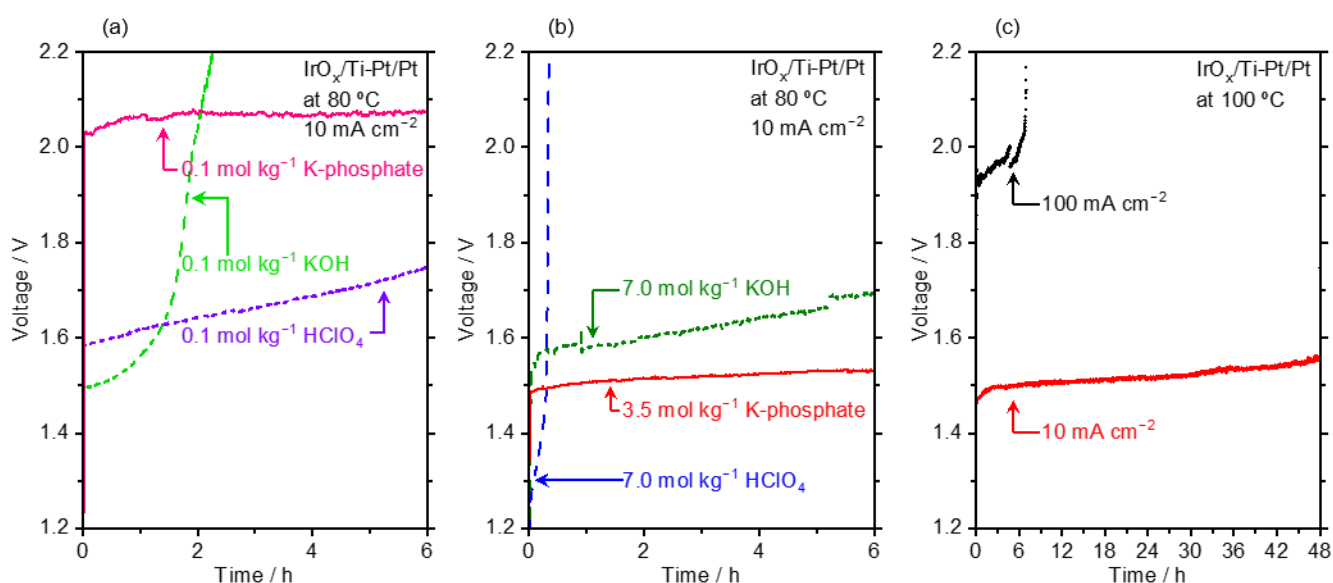


**Figure S7.** Surface morphology of Pt/Pt mesh. SEM images of (a) bare Pt mesh, (b) fresh Pt/Pt mesh, and (c) used Pt/Pt mesh electrodes. All figures on the left were taken in high resolution, and the corresponding images at lower magnification are shown on the right.

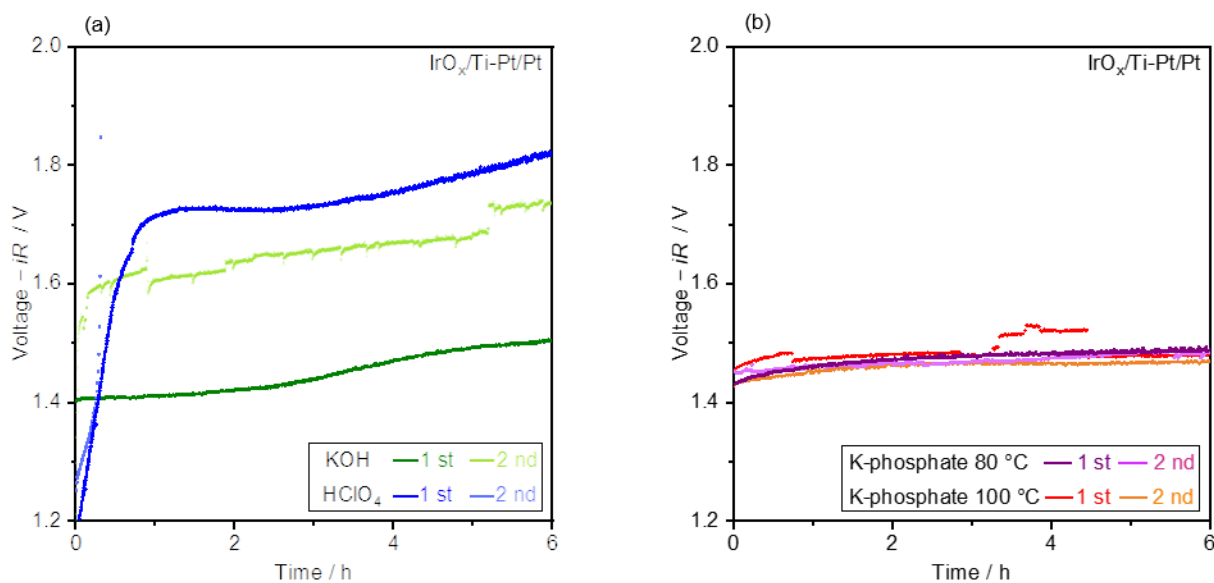




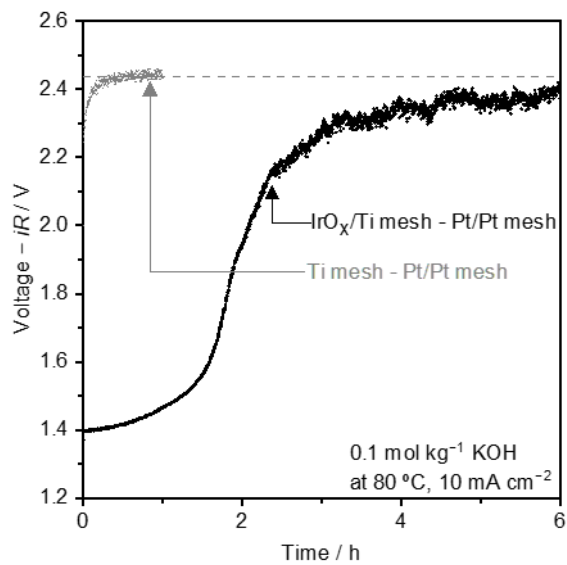
**Figure S8.** The scheme of the two-electrode cell configuration. The cell at elevated temperatures up to 80 °C was equipped with a jacket, and its temperature was controlled by an external equipment. For testing above 80 °C, the temperature was controlled by placing the cell in the oil bath. 550 mm quartz glass tubes were used for vapor reflux. Platinum wires were passed through the glass tube and connected to the electrodes. Ar gas was bubbled into the electrolyte without stirring. For simplicity, the gas flow path is not described.



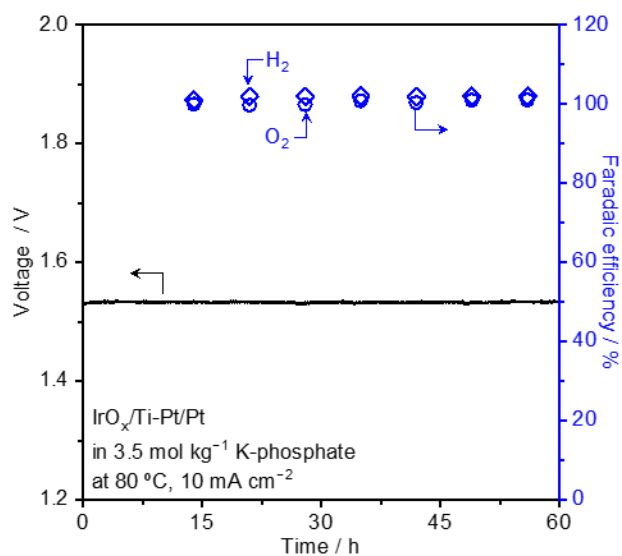
**Figure S9.** Water electrolysis performance in densely buffered solutions without  $iR$ -correction corresponding to **Figure 5**. (a) Chronopotentiometry (CP) profile performed at  $10 \text{ mA cm}^{-2}$  and  $80 \text{ }^\circ\text{C}$  in electrolyte solutions of  $0.1 \text{ mol kg}^{-1}$  KOH,  $0.1 \text{ mol kg}^{-1}$  HClO<sub>4</sub>, and  $0.1 \text{ mol kg}^{-1}$  K-phosphate. (b) CP profile performed at  $10 \text{ mA cm}^{-2}$  and  $80 \text{ }^\circ\text{C}$  in electrolyte solutions of  $7.0 \text{ mol kg}^{-1}$  KOH,  $7.0 \text{ mol kg}^{-1}$  HClO<sub>4</sub>, and  $3.5 \text{ mol kg}^{-1}$  K-phosphate. These profiles are the average of the experiments for  $3.5 \text{ mol kg}^{-1}$  K-phosphate,  $7.0 \text{ mol kg}^{-1}$  HClO<sub>4</sub>, and KOH (c) Overall water electrolysis performance was accessed by CP at  $10$  and  $100 \text{ mA cm}^{-2}$  in  $4.1 \text{ mol kg}^{-1}$  K-phosphate solutions at  $100 \text{ }^\circ\text{C}$ . All measurements were performed in the two-electrode configuration using IrO<sub>x</sub>/Ti mesh and Pt/Pt mesh as anode and cathode with a geometric surface area of  $1.0 \text{ cm}^2$ , respectively, under Ar bubbling. The pH level of K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements.



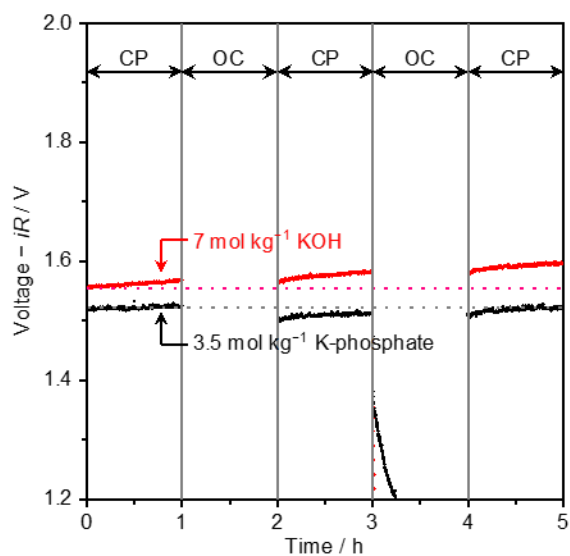
**Figure S10.** Raw data of the water electrolysis performance. Chronopotentiometry (CP) profiles at  $10 \text{ mA cm}^{-2}$  were recorded with Ar bubbling in electrolyte solutions of (a)  $7.0 \text{ mol kg}^{-1} \text{ HClO}_4$  and  $7.0 \text{ mol kg}^{-1} \text{ KOH}$  at  $80 \text{ }^\circ\text{C}$  as well as (b) K-phosphate of  $3.5 \text{ mol kg}^{-1}$  at  $80 \text{ }^\circ\text{C}$  and of  $4.1 \text{ mol kg}^{-1}$  at  $100 \text{ }^\circ\text{C}$ . The voltage displayed in the figure has been  $iR$ -corrected with measured impedance value. The raw data shown herein were used to prepare the figure displayed in **Figure 5a**. Each measurement was performed twice with newly prepared electrodes. The pH level of K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements.



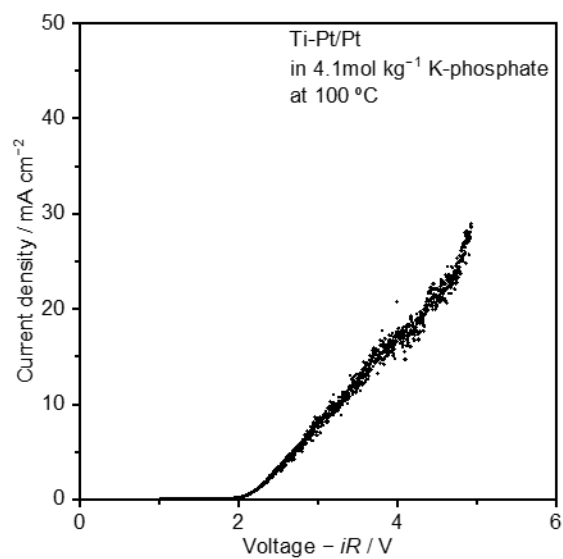
**Figure S11.** Water electrolysis performance in KOH. CP profiles at  $10 \text{ mA cm}^{-2}$  were obtained in the two-electrode configuration using  $\text{IrO}_x/\text{Ti}$  mesh anode and Pt/Pt mesh cathode as well as Ti mesh anode and Pt/Pt mesh cathode. These measurements were conducted in  $0.1 \text{ mol kg}^{-1}$  KOH solution at  $80 \text{ }^\circ\text{C}$ . The voltage displayed in the figure has been  $iR$ -corrected with measured impedance value.



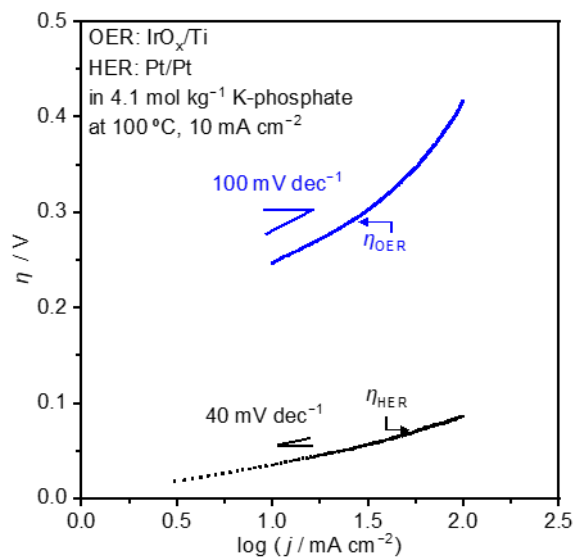
**Figure S12.** Demonstration of water electrolysis in densely buffered solutions at neutral pH. Overall water electrolysis performance was accessed by CP at 10 mA cm<sup>-2</sup> in K-phosphate solutions of 3.5 mol kg<sup>-1</sup> at 80 °C in the two-electrode configuration using a IrO<sub>x</sub>/Ti mesh anode and a Pt/Pt mesh cathode with Ar bubbling. The evolved gases were detected by on-line gas chromatograph equipped with thermal conductivity detector. The pH level of K-phosphate solutions was adjusted to 7.0 at 25 °C prior to the measurements.



**Figure S13.** On-off cycling of water electrolysis in densely buffered solutions. On-off testing results were obtained by periodic CP at  $10 \text{ mA cm}^{-2}$  for 1 h with an interval of 1 h at open-circuit (OC) condition in  $7.0 \text{ mol kg}^{-1}$  KOH and  $3.5 \text{ mol kg}^{-1}$  K-phosphate (pH 7.0) at  $80 \text{ }^\circ\text{C}$ . The measurement was performed after CP for 6 h shown in **Figure 5b**. The voltage displayed in the figure has been  $iR$ -corrected with measured impedance value. The pH level of K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements

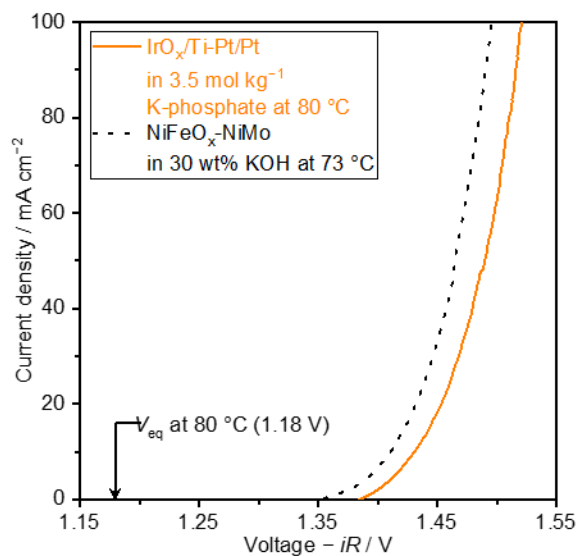


**Figure S14.** Water electrolysis performance using Ti mesh anode at the neutral pH. CV profiles at a scan rate of  $10 \text{ mV s}^{-1}$  were recorded in K-phosphate solutions of  $4.1 \text{ mol kg}^{-1}$  at  $100 \text{ }^\circ\text{C}$  in the two-electrode configuration using a Ti mesh anode and a Pt/Pt mesh cathode with Ar bubbling. The pH level of K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements. The voltage displayed in the figure has been  $iR$ -corrected with the measured impedance value.

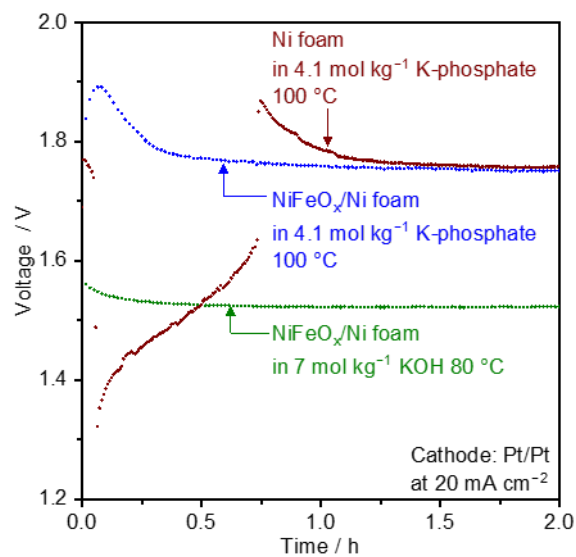


**Figure S15.** Tafel plots of the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) over Pt/Pt mesh and IrO<sub>x</sub>/Ti mesh, respectively. All measurements were recorded by CP measurement at a scan rate of 10 mV s<sup>-1</sup> in 4.1 mol kg<sup>-1</sup> K-phosphate at 100 °C in the three-electrode configuration with Hg/Hg<sub>2</sub>Cl<sub>2</sub> (saturated KCl) reference electrode. The pH of the K-phosphate solutions was adjusted to 7.0 at 25 °C prior to the measurements.





**Figure S16.** Cyclic voltammograms recorded at a scan rate of  $10 \text{ mV s}^{-1}$  in K-phosphate of  $3.5 \text{ mol kg}^{-1}$   $80 \text{ }^\circ\text{C}$  in the two-electrode configuration.  $V_{\text{eq}}$  denotes equilibrium voltage for water electrolysis. The current-voltage relationship over the NiFeO<sub>x</sub>/Ni foam anode and NiMo/Ni foam cathode in 30 wt% KOH at  $73 \text{ }^\circ\text{C}$  is also presented in the figure, which was adopted from our previous study.<sup>[S2]</sup> All measurements were performed in the two-electrode configuration using IrO<sub>x</sub>/Ti mesh and Pt/Pt mesh as anode and cathode, respectively, under Ar bubbling. The voltage displayed in the figure has been  $iR$ -corrected with measured impedance value. The pH level of K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements.



**Figure S17.** Water electrolysis performance using Ni-based materials as anode. CP profile at  $20 \text{ mA cm}^{-2}$  were recorded in  $4.1 \text{ mol kg}^{-1}$  K-phosphate solution at  $100 \text{ }^\circ\text{C}$  in the two-electrode configuration using  $\text{NiFeO}_x/\text{Ni}$  foam anode or Ni foam anode, together with the Pt/Pt cathode under Ar bubbling. As a control experiment, a CP profile was obtained in  $7.0 \text{ mol kg}^{-1}$  KOH solution at  $80 \text{ }^\circ\text{C}$  using the  $\text{NiFeO}_x/\text{Ni}$  foam anode and the Pt/Pt cathode. The pH level of the K-phosphate solutions was adjusted to 7.0 at  $25 \text{ }^\circ\text{C}$  prior to the measurements.

**Table S1.** Viscosity of phosphate solutions at the neutral pH. Viscosity of Na-, K-, and Cs-phosphate solutions was measured at various temperatures using a viscometer, and pH levels of solutions were adjusted to 7.0 at 25 °C prior to the measurements.

		Viscosity / mPa s								
	Molality / mol kg <sup>-1</sup>	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
Na-phosphate	0.05	0.87								
	0.10	0.91	0.81	0.66	0.55	0.47				
	0.20	0.90								
	0.30	1.01								
	0.40	1.06								
	0.50	1.10								
	0.60	1.24								
	0.75	1.36								
	0.90	1.60	1.43	1.15	0.95	0.80				
	1.80		2.90	2.22	1.78	1.46				
	2.00			3.62	2.71	2.13	1.75	1.57	1.31	1.14
	2.50			4.69	3.52	2.74	2.21			
4.60									7.92	
K-phosphate	0.10	0.91								
	0.20	1.04								
	0.50	0.95	0.86	0.69	0.56	0.49				
	0.75	1.14								
	0.90	1.27	1.14	0.94	0.79	0.67				
	1.25	1.64								
	1.50	1.87	1.67	1.37	1.14	0.98				
	1.70	1.98	1.78	1.46	1.22	1.04				
	2.00	2.52	2.27	1.89	1.52	1.28	1.09	0.99	0.85	0.8
	2.80	3.84	3.42	2.72	2.24	1.87				

		Viscosity / mPa s								
	Molality / mol kg <sup>-1</sup>	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C	100 °C
K-phosphate	3.70				4.98	4.06	3.39	2.88	2.46	2.14
	4.10									2.88
Cs-phosphate	0.1	0.95								
	0.25	0.92								
	0.33	1.02								
	0.50	0.93	0.83	0.68	0.67	0.55				
	0.75	1.14								
	1.00	1.32								
	1.40	1.86	1.68	1.40	1.18	1.02				
	1.70	2.45	2.14	1.84	1.53	1.31				
	2.00	3.76	3.41	2.86	2.33	1.96	1.70	1.55	1.29	1.14
	2.20	4.39	3.96	3.23	2.70	2.26				

## Reference

- [S1] W.M. Haynes, D.R. Lide, *Handbook of Chemistry and Physics, 92nd ed.*, CRC Press, Boca Raton, FL, **2011**
- [S2] T. Shinagawa, M. T.-K. Ng, K. Takanabe, *Angew. Chem. Int. Ed.* **2017**, *56*, 5061-5065.