

# Supporting Information

## **Tetraruthenium Polyoxometalate as an Atom-Efficient Bifunctional OER/ORR Catalyst and Its Application in Seawater Batteries**

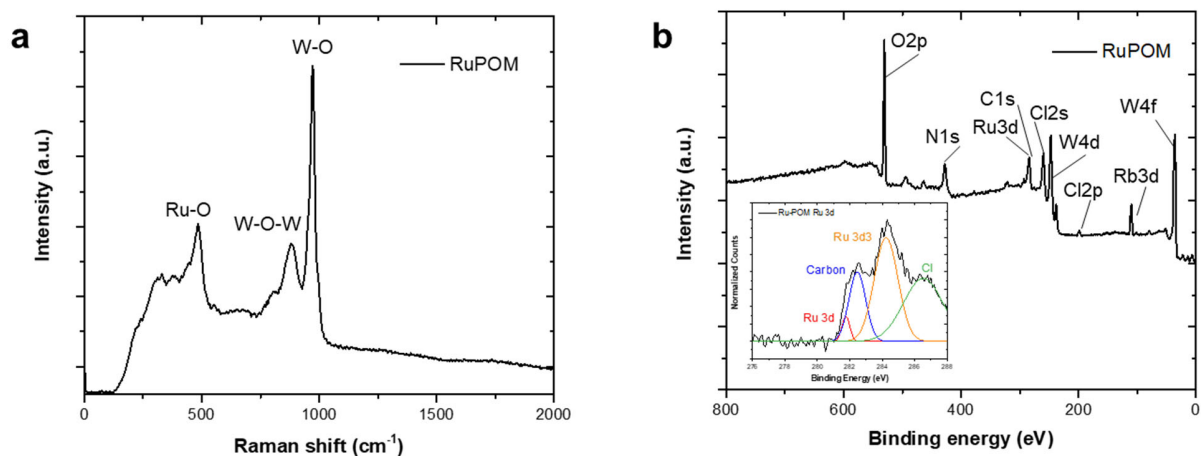
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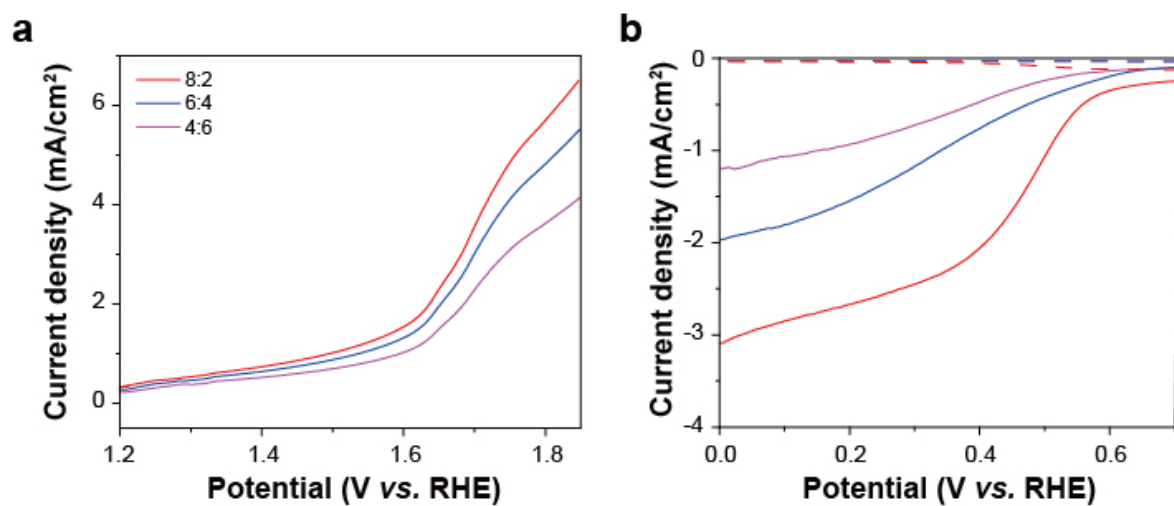
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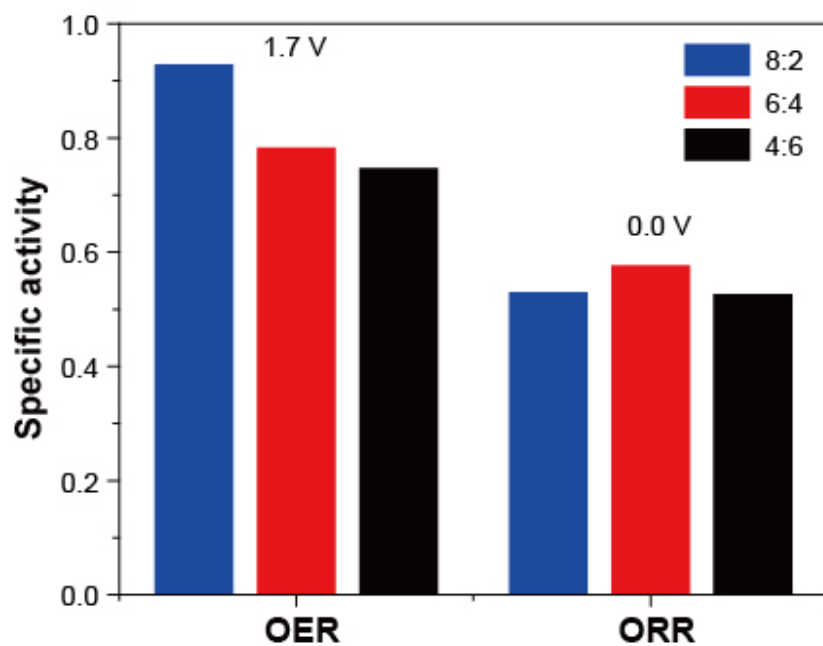
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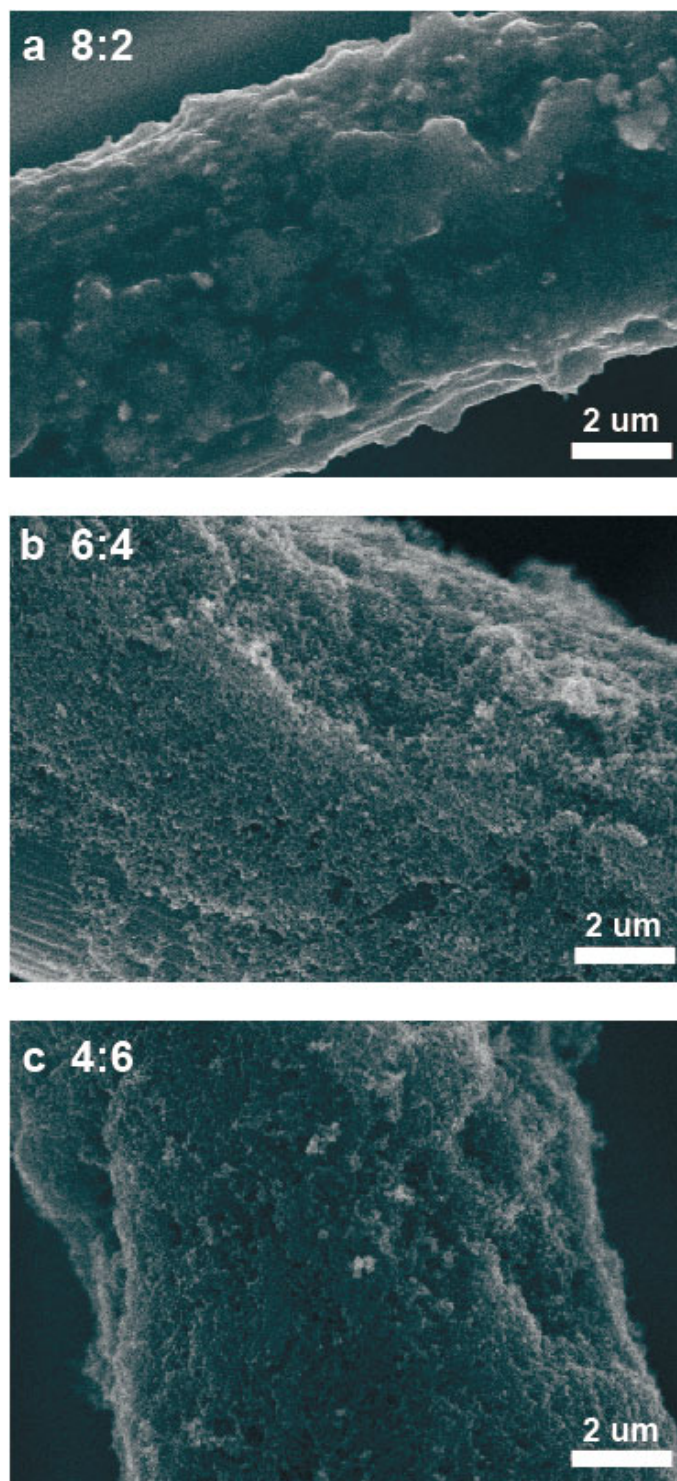
**Figure S1.** (a) Raman and (b) XPS spectra of RuPOM prepared according to the literature.<sup>22,24</sup> The inset shows Ru 3d and C 1s XPS spectra.



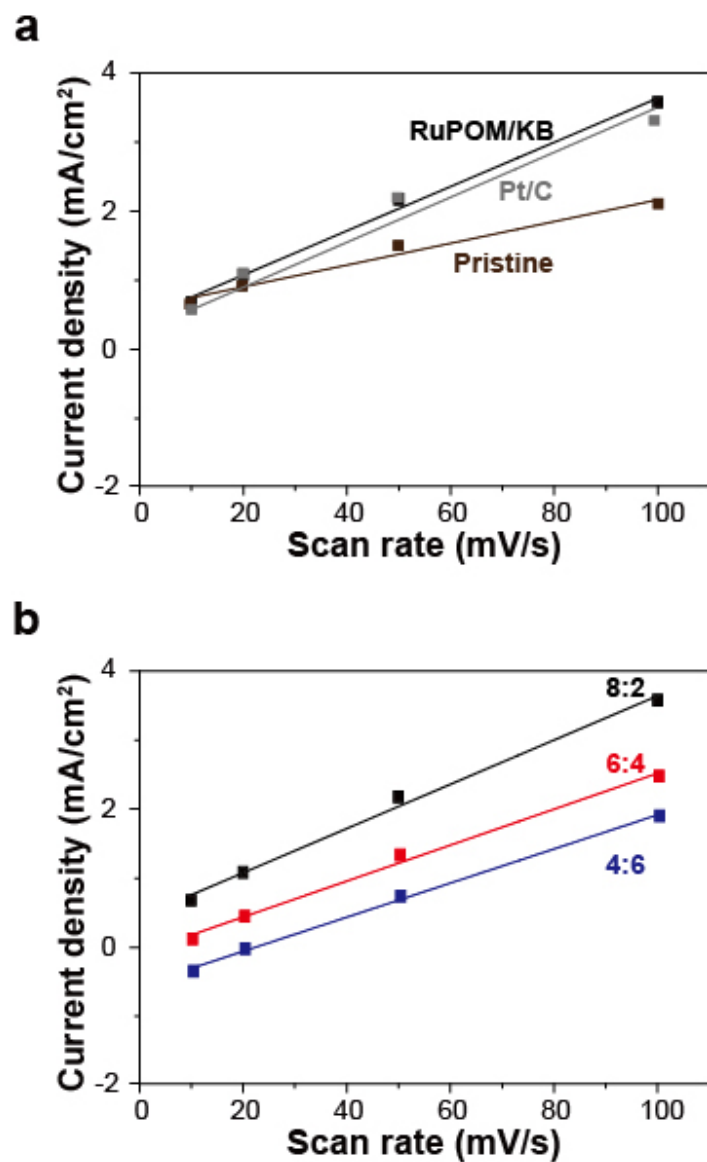
**Figure S2.** Electrocatalytic activity of RuPOM/KB at different mass ratios (RuPOM : KB). (a) OER and (b) ORR polarization curves of the respective samples at a scan rate of  $10 \text{ mV s}^{-1}$ . OER and ORR activity was evaluated in  $\text{N}_2$ - and  $\text{O}_2$ -saturated seawater, respectively. For the ORR test, an RRDE was employed at 1200 rpm.



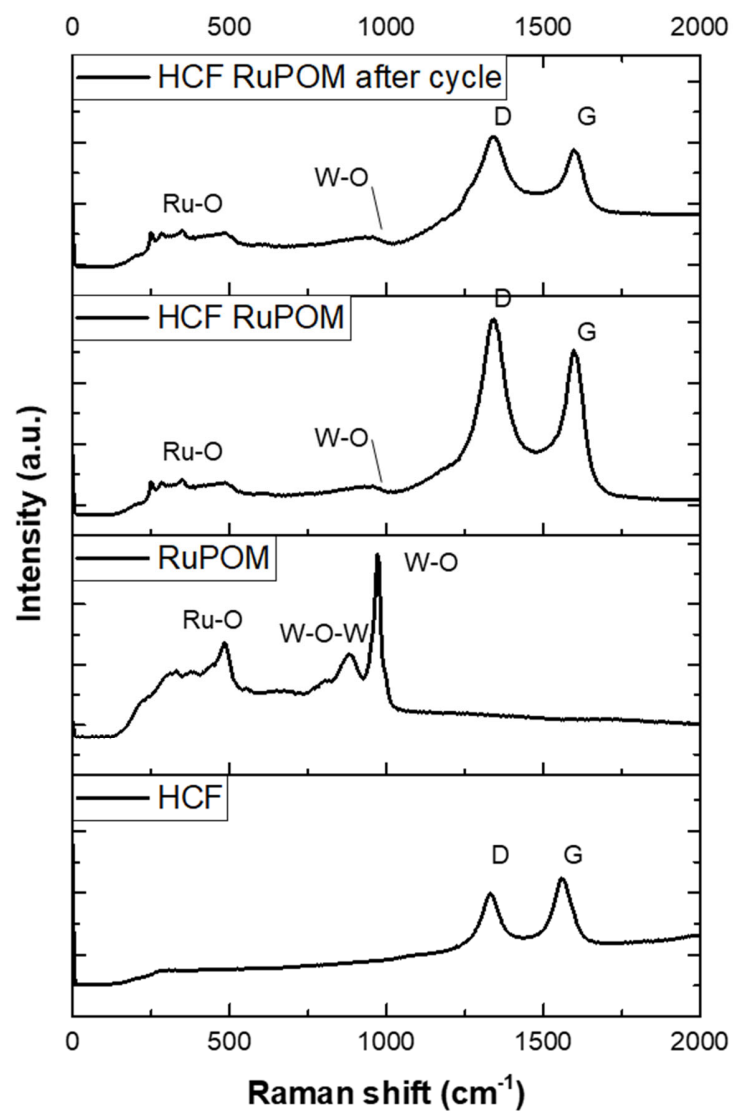
**Figure S3.** Comparison between specific catalytic activities of the RuPOM/KB mixtures with different mass ratios between RuPOM and KB for OER and ORR.



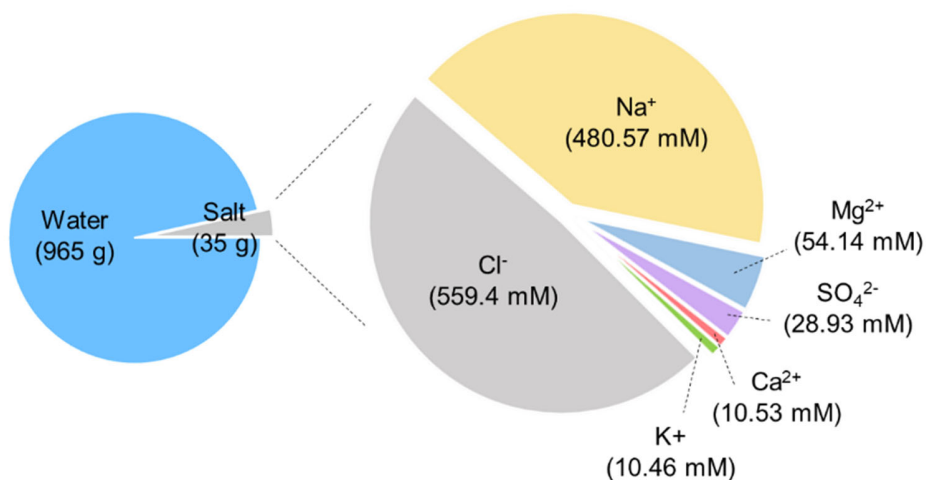
**Figure S4.** SEM images of HCF coated with RuPOM/KB at different mass ratios (RuPOM : KB). (a) 8:2, (b) 6:4, and (c) 4:6.



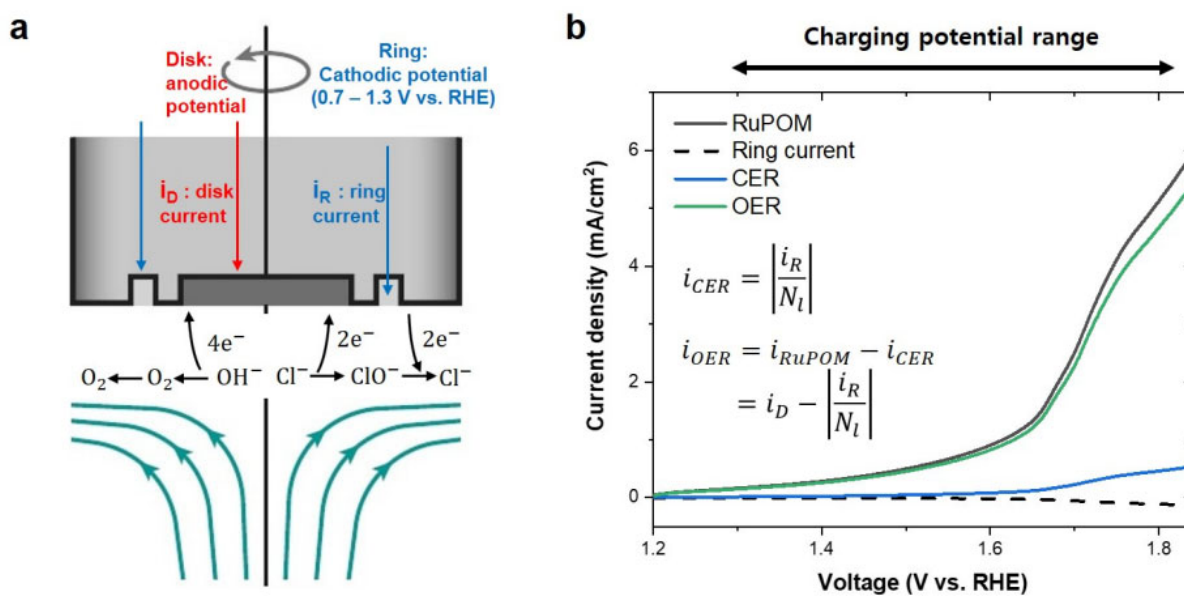
**Figure S5.** Scan rate vs. current density plots for the determination of electrochemically active surface area of electrodes. Cyclic voltammograms were measured at different scan rates in seawater. (a) Comparison between HCF electrodes with and without modification (i.e., pristine) with Pt/C or RuPOM/KB (8:2). (b) Comparison between HCFs modified with RuPOM/KB at different mass ratios.



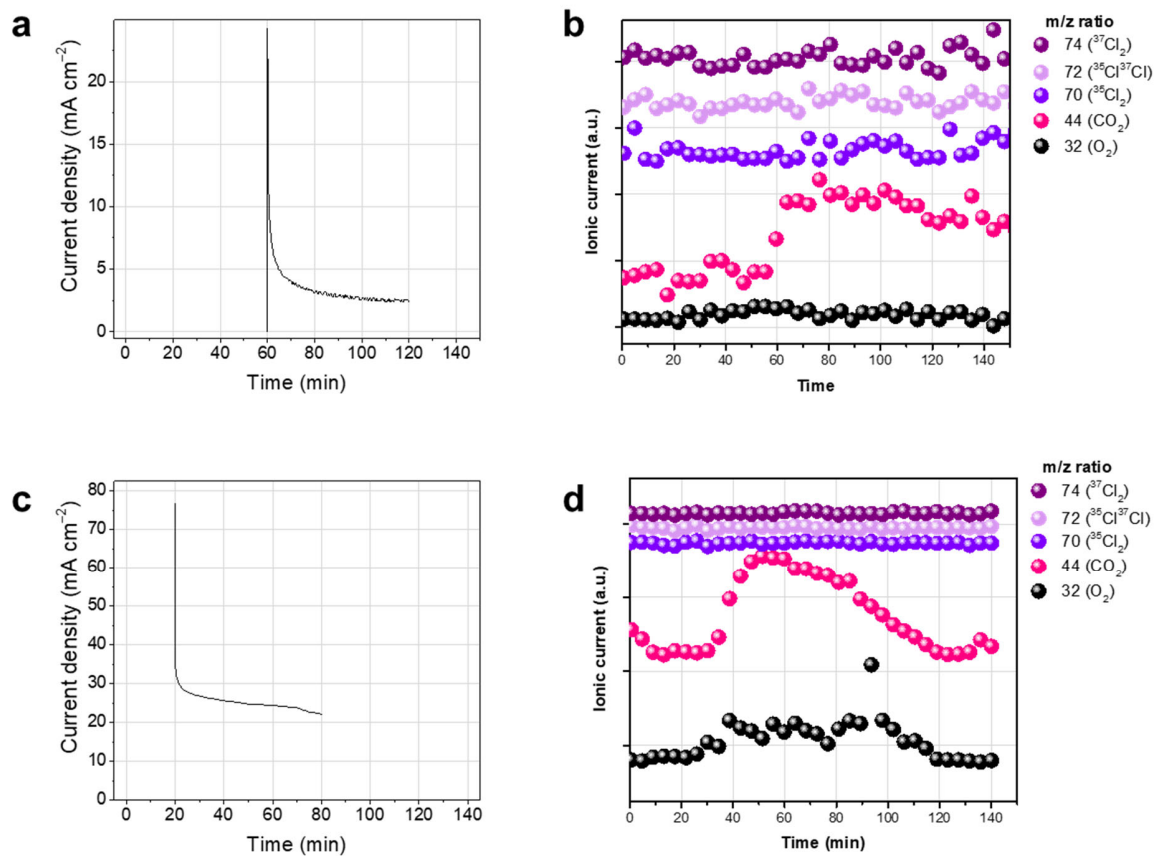
**Figure S6.** Raman spectra of the pristine HCF, RuPOM, and HCF with RuPOM/KB. The HCF with RuPOM/KB was also analyzed after 50 cycles of charging and discharging.



**Figure S7.** Chemical composition of seawater. Seawater batteries employ  $\text{Na}^+$  ions in seawater upon charging and discharging, as shown in Figure 1b.



**Figure S8.** Measurement of competition between OER and CER using RRDE voltammetry. (a) Experimental scheme. (b) RRDE voltammograms showing each contribution of OER and CER to the overall current from seawater oxidation.



**Figure S9.** DEMS analysis of gas evolution by RuPOM in (a-b) the absence and (c-d) presence of RuPOM/KB upon the oxidation of seawater: (a, c) Chronoamperograms and (b, d) corresponding mass spectra. For DEMS analysis, an H cell (working & reference electrode | Nafion | counter electrode) was used in seawater at 1.4 V vs. RHE.



**Table S1.** Performance of HCF air cathodes modified with different RuPOM/KB samples for SWB. For comparison.

RuPOM:KB mass ratio	Current density	Charging voltage	Discharging voltage	Potential gap
Pristine	0.1 mA/cm <sup>2</sup>	3.962	2.660	1.302
	0.2 mA/cm <sup>2</sup>	4.253	2.652	1.601
	0.5 mA/cm <sup>2</sup>	4.421	2.641	1.780
RuPOM:KB (8:2)	0.1 mA/cm <sup>2</sup>	3.602	2.841	0.761
	0.2 mA/cm <sup>2</sup>	3.661	2.805	0.856
	0.5 mA/cm <sup>2</sup>	3.859	2.778	1.082
RuPOM:KB (6:4)	0.1 mA/cm <sup>2</sup>	3.621	2.804	0.818
	0.2 mA/cm <sup>2</sup>	3.719	2.753	0.966
	0.5 mA/cm <sup>2</sup>	3.928	2.654	1.273
RuPOM:KB (4:6)	0.1 mA/cm <sup>2</sup>	3.645	2.768	0.877
	0.2 mA/cm <sup>2</sup>	3.754	2.696	1.057
	0.5 mA/cm <sup>2</sup>	3.945	2.610	1.335