Supplementary Data

## *In-situ* **desalination-coupled electrolysis with concurrent one-step-synthesis**

## **of value-added chemicals**

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Sample	Element	Elemental fraction $(\%)$		
		<b>XPS</b>	<b>SEM-EDS</b>	<b>STEM</b>
As-deposited	Ni	73.6	31.2	68.4
NiFe-LDH	Fe	26.4	68.8	31.6
Post-anodized	Ni	66.9	34.3	70.2
NiFe-LDH	Fe	33.1	65.7	29.8
NiMo	Ni	81.7	89.6	
	Mo	18.3	10.4	

**Table S1**. Elemental (metal) fractions of NiFe-LDH and NiMo catalysts estimated by XPS, SEM-EDS, and STEM.

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**Table S2**. Performance comparison of water splitting catalysts in literature.



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Figure S1. N<sub>2</sub> adsorption and desorption isotherms of (a) as-deposited NiFe-LDH (AD-NiFe), (b) post-anodized NiFe-LDH (PA-NiFe), (c) NiMo, and (d) Ni substrate.



**Figure S2.** Pore diameter distributions of (a) as-deposited NiFe (AD-NiFe), (b) post-anodized NiFe (PA-NiFe), (c) NiMo, and (d) Ni substrate.



**Figure S3.** (a) Specific surface areas (BET method), (b) average pore diameters (BJH method), and (c) electrochemical double-layer capacitance (Cdl) of as-deposited NiFe-LDH (AD-NiFe), post-anodized NiFe (PA-NiFe), NiMo, and Ni substrate. Electrolytes for NiFe and Ni substrate: 1 M KOH. Electrolyte for NiMo: 1 M H<sub>2</sub>SO<sub>4</sub>. C<sub>dl</sub> of NiMo was not obtained due to high Faradaic currents in the acidic solution.



**Figure S4.** Linear sweep voltammograms of NiFe-LDH electrodes deposited at various Ni/Fe ratios and deposition time.



**Figure S5.**  $\eta$  values with NiFe-LDH electrodes for OER at (a)  $J = 10$  mA cm<sup>-2</sup> and (b)  $J = 100$ mA cm<sup>-2</sup> ( $\eta_{10}$  and  $\eta_{100}$ , respectively).



**Figure S6.** Changes in  $E_{\text{device}}$  and electrolyte pH values with time at  $J = 10 \text{ mA cm}^{-2}$  in twocell devices divided by BPMs with anolyte of 1 M KOH and catholyte of 1 M H<sub>2</sub>SO<sub>4</sub>. (a) NiFe-LDH anode and NiMo cathode pair, (b) Pt anode-Pt cathode pair, and (c) Ni anode-Ni cathode pair.



**Figure S7**. Changes in *E*device and electrolyte pH values with NiFe-LDH anode and NiMo cathode pairs in two-cell devices divided by (a) an AEM, (b) a CEM, and (c) a PEM with anolyte of 1 M KOH and catholyte of 1 M H<sub>2</sub>SO<sub>4</sub> at  $J = 100$  mA cm<sup>-2</sup>.



**Figure S8.** A desalination-coupled electrocatalytic unit device with NiFe-LDH anode and NiMo cathode at  $J = 10$  mA cm<sup>-2</sup> (Case Study II in Table 1). The device configuration is the same as that of Case Study I, except for acid cell (0.2 M NaCl) and base cell (0.2 M NaCl). For the device construction, see Scheme 1b. (a) Changes in  $E_{\text{device}}$  and ionic conductivity ( $\sigma$ ) of saline water with electrolysis time. (b) Changes in concentrations of desalted ions (Cl<sup>-</sup> and Na<sup>+</sup>). (c) Changes in pH values in the solutions in the acid and base cells, and electrolytes.



**Figure S9.** A desalination-coupled electrocatalytic unit device with NiFe-LDH anode and NiMo cathode at  $J = 10$  mA cm<sup>-2</sup> (Case Study III in Table 1). The device configuration is the same as that of Case Study I, except for acid cell (0.1 M HCl) and base cell (0.1 M NaOH). For the device construction, see Scheme 1b. (a) Changes in  $E_{\text{device}}$  and ionic conductivity ( $\sigma$ ) of saline water with electrolysis time. (b) Changes in concentrations of desalted ions (Cl<sup>-</sup> and Na<sup>+</sup>). (c) Changes in pH values in the solutions in the acid and base cells, and electrolytes.



**Figure S10.** A desalination-coupled electrocatalytic unit device with NiFe-LDH anode and NiMo cathode at  $J = 100$  mA cm<sup>-2</sup> (Case Study IV in Table 1). The other conditions are the same as those in Figure S9. (a) Changes in  $E_{\text{device}}$  and ionic conductivity ( $\sigma$ ) of saline water with electrolysis time. (b) Changes in concentrations of desalted ions (Cl<sup>-</sup> and Na<sup>+</sup>). (c) Changes in pH values in the solutions in the acid and base cells, and electrolytes.



**Figure S11.** A five-desalination cell array-coupled electrocatalysis with desalination cell (seawater, salinity 36  $g L^{-1}$ ). For device configuration and conditions, refer to Case Study VI in Table 1. (a) Changes in  $E_{\text{device}}$  and ionic conductivity  $(\sigma)$  of saline water with electrolysis time. The dashed line represents the theoretical  $\sigma$  based on *J*. (b) Changes in concentrations of desalted ions ( $Cl<sup>-</sup>$  and Na<sup>+</sup>). The dashed line represents the theoretical  $Cl<sup>-</sup>$  concentration in the acid cell. (c) Changes in pH values in the solutions in the acid and base cells, and electrolytes.