

## Supporting Information

### **Thin-film composite membranes for hydrogen evolution with a saline catholyte water feed**

Le Shi<sup>1,2\*</sup>, Xuechen Zhou<sup>1</sup>, Rachel Taylor<sup>3</sup>, Chenghan Xie<sup>1</sup>, Bin Bian<sup>1</sup>, Derek M. Hall<sup>4</sup>, Ruggero Rossi<sup>1,6</sup>,  
Michael A. Hickner<sup>5</sup>, Christopher A. Gorski<sup>1</sup>, & Bruce E. Logan<sup>1,3\*</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, 16801, USA

<sup>2</sup>College of Environmental and Resource Sciences, Zhejiang University, Hangzhou, 310058, P.R.China

<sup>3</sup>Department of Chemical Engineering, The Pennsylvania State University, University Park, PA, 16801, USA

<sup>4</sup>Department of Mechanical Engineering, The Pennsylvania State University, University Park, PA, 16801, USA

<sup>5</sup>Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA, 16801, USA

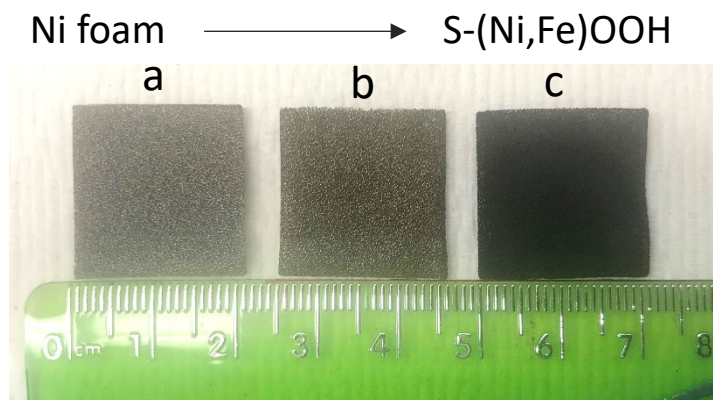
<sup>6</sup>Department of Environmental Health and Engineering, Johns Hopkins University, Baltimore, MD, 21218, USA

\*Corresponding author Email: [blogan@psu.edu](mailto:blogan@psu.edu); Tel.: +1-814-863-7908; [le.shi@zju.edu.cn](mailto:le.shi@zju.edu.cn)

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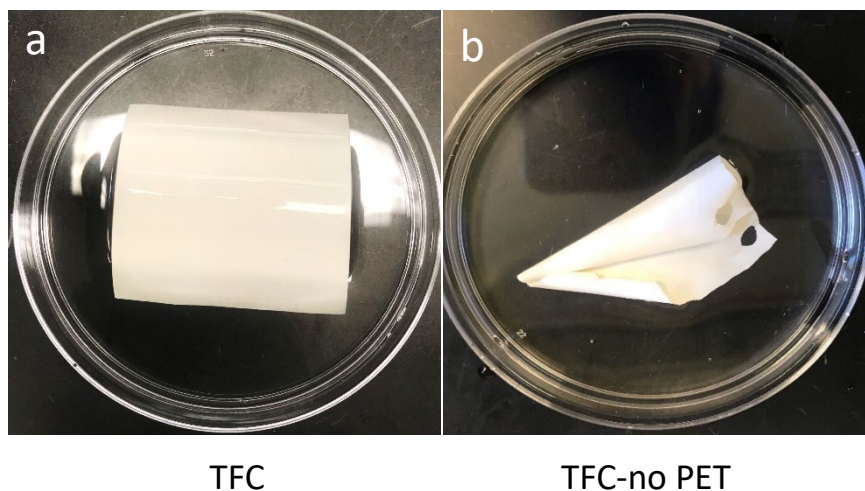
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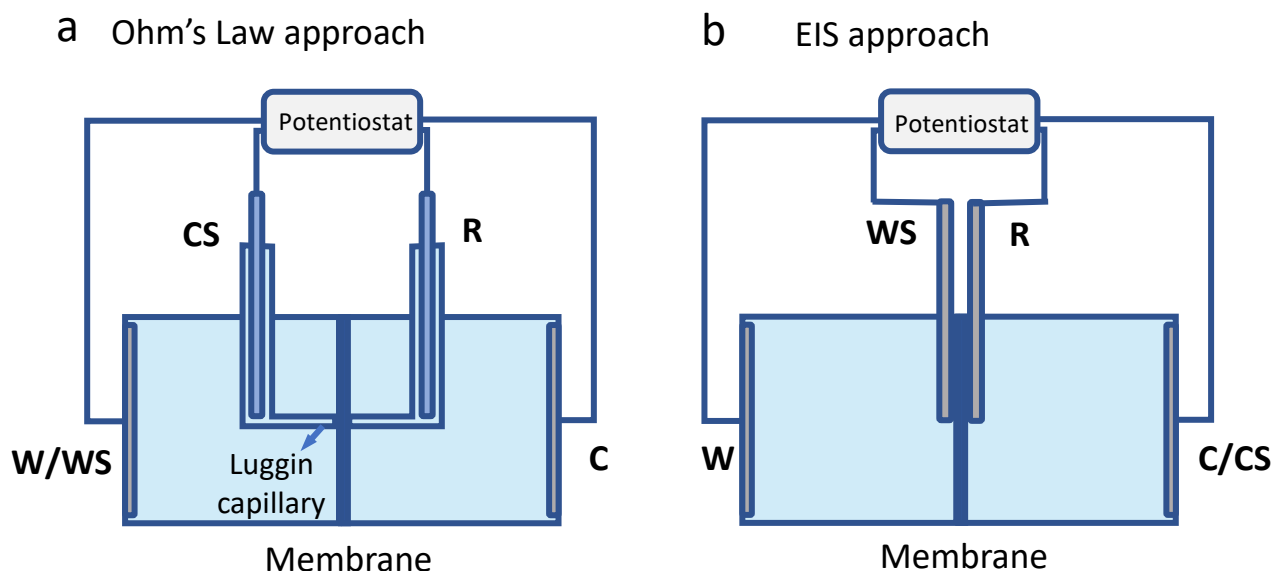


S-doped Ni/Fe(oxy)hydroxide electrodes

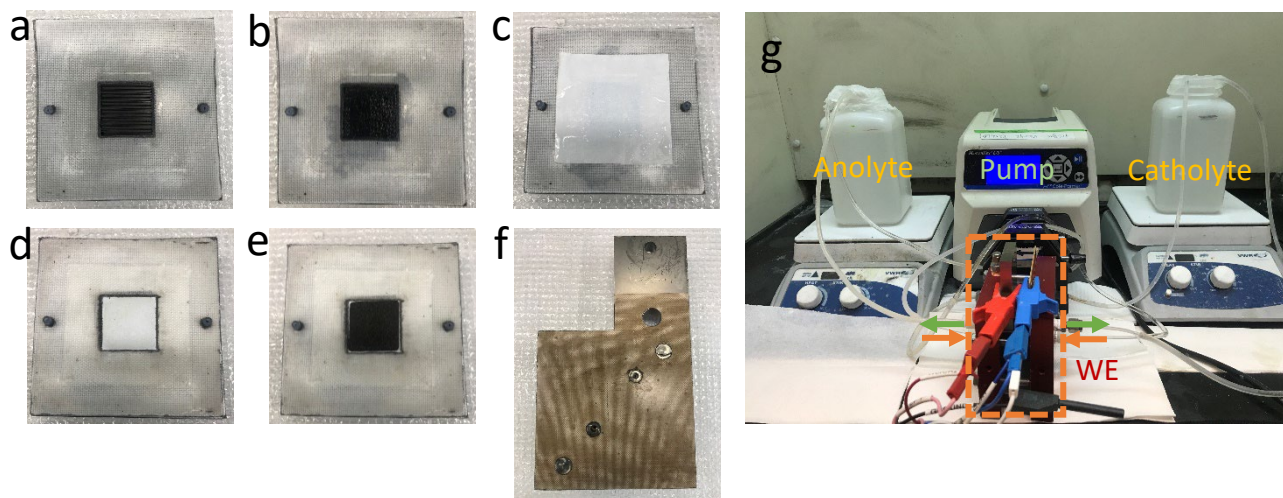
**Figure S1.** Photograph of (a) Ni foam and S-(Ni,Fe)OOH electrodes prepared under different preparation conditions (b) without shaking and (c) with shaking during reaction for 5 min.



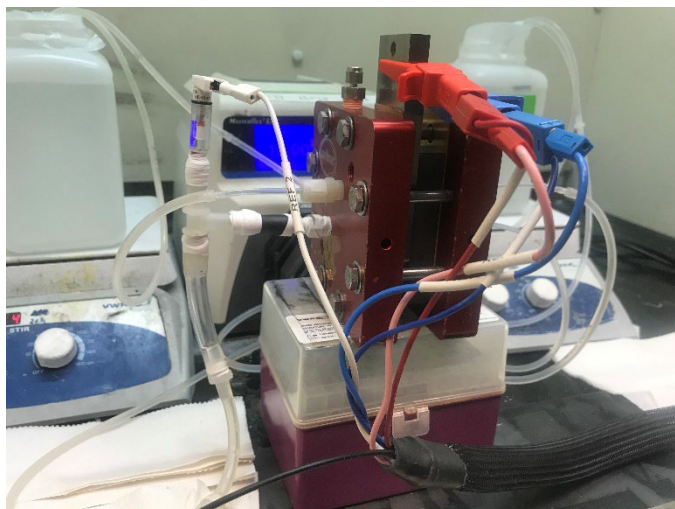
**Figure S2.** Photographs of (a) BW30XLE (TFC), and (b) BW30XLE after PET layer removal immersed in DI water (TFC-no PET).



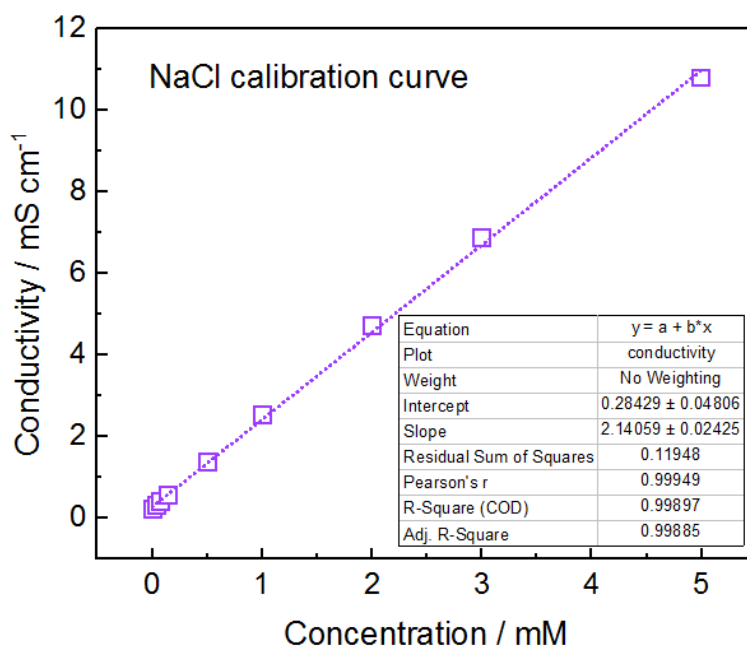
**Figure S3.** Schematic of working electrode (W), Working sense (WS), Reference electrode (R), Counter electrode (C) and Counter sense (CS) connection in 4-electrode measurement set-up for: (a) Ohm's Law approach and (b) EIS approach.



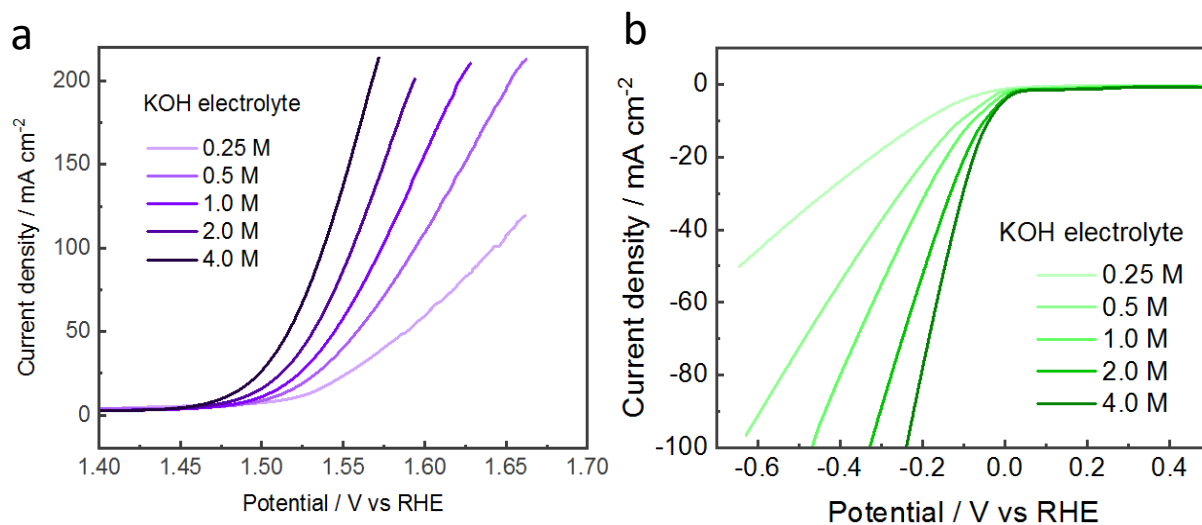
**Figure S4.** Assembly of the electrolyzer: (a) gasket with graphite endplate with serpentine flow channels; (b) 10% Pt/C coated carbon cloth is placed on the flow channels as the cathode; (c) TFC-no PET membrane is placed on the gasket with active layer facing the cathode; (d) another gasket is placed on the membrane with a fabric spacer in the open area; (e) the pre-pressed S-(Ni,Fe)OOH/Ni foam is placed on the spacer as the anode; (f) the other platinized Ti plate is placed on the anode side and further tightened with a torque wrench (9 Nm). (g) Photograph of water electrolyzer set-up for performance test with alkaline catholyte and anolyte pumping with a peristaltic pump.



**Figure S5.** Photograph of water electrolyzer set-up with addition of Hg/HgO reference electrode in the inlet of anode chamber for overpotential contribution analysis.



**Figure S6.** A linear calibration curve of conductivity vs NaCl concentration of the flow-through conductivity electrodes (ET908 Flow-Thru Conductivity Electrode, eDAQ).



**Figure S7.** LSV measurements for (a) the S-(Ni,Fe)OOH electrode tested in KOH as alkaline electrolytes with different concentrations for OER, (b) the Pt/C electrodes tested in KOH as alkaline electrolytes with different concentrations for HER. All these curves presented without  $iR$  correction.

**Table S1.** Osmotic pressure calculation of different electrolyte conditions

Conditions	Parameter	Anolyte	Catholyte
A: 0.5 M KOH – C: 0.5 M KOH	$\varphi$	0.948	0.948
	$\pi$ / bar	23.459	23.459
A: 2.0 M KOH – C: 0.5 M NaOH	$\varphi$	1.123	0.928
	$\pi$ / bar	111.161	22.965

Osmotic pressure of difference electrolytes can be calculated based on modified Van't Hoff equation:

$$\pi = i\varphi_c RTC$$

where  $\pi$  is the osmotic pressure,  $i$  is the Van't Hoff factor ( $i = 2$  for KOH, NaOH and NaCl),  $\varphi_c$  is the osmotic coefficient,  $C$  is the molar concentration of solute,  $R = 0.083 \text{ L bar moles}^{-1}\text{K}^{-1}$  is the gas constant,  $T = 298.15 \text{ K}$  is the absolute temperature.<sup>1</sup>

### Water volume change due to water splitting

When applying  $100 \text{ mA/cm}^2$  ( $400 \text{ mA}$ ) for  $20 \text{ h}$ , if Faraday efficiency is  $100 \%$ , produced moles of  $\text{H}_2$  ( $n_{\text{CE}}$ ):

$$n_{\text{CE}} = \frac{\int_{i=1}^n I_i \Delta t}{2F} = \frac{400 \times 0.001 \text{ A} \times 72000 \text{ s}}{2 \times 96485 \text{ C/mol}} = 0.1492 \text{ mol}$$

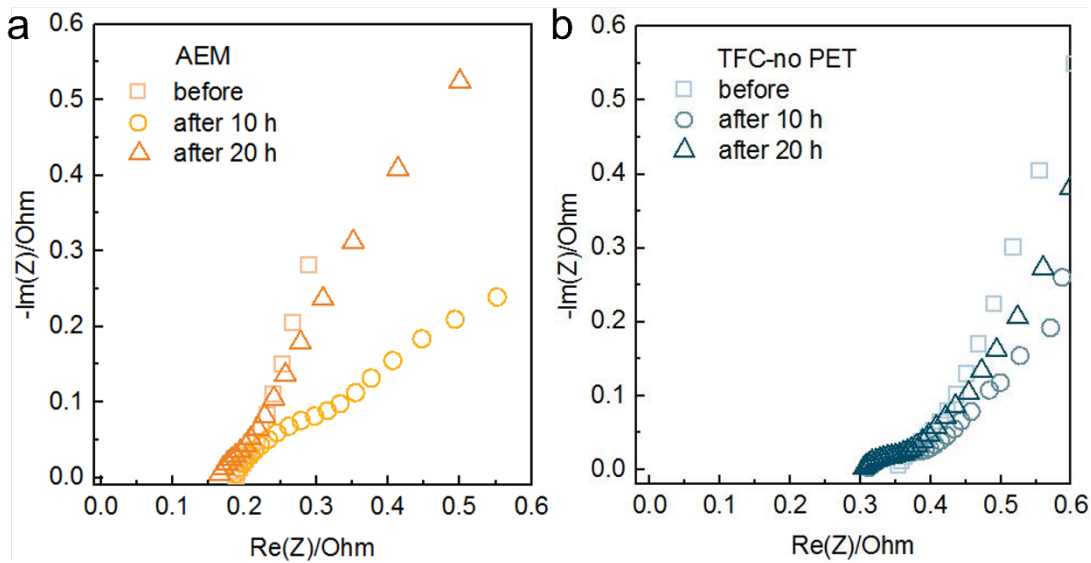
produced moles of  $\text{O}_2$  ( $n_{\text{CE}}$ ):

$$n_{\text{CE}} = \frac{\int_{i=1}^n I_i \Delta t}{4F} = 0.0746 \text{ mol}$$

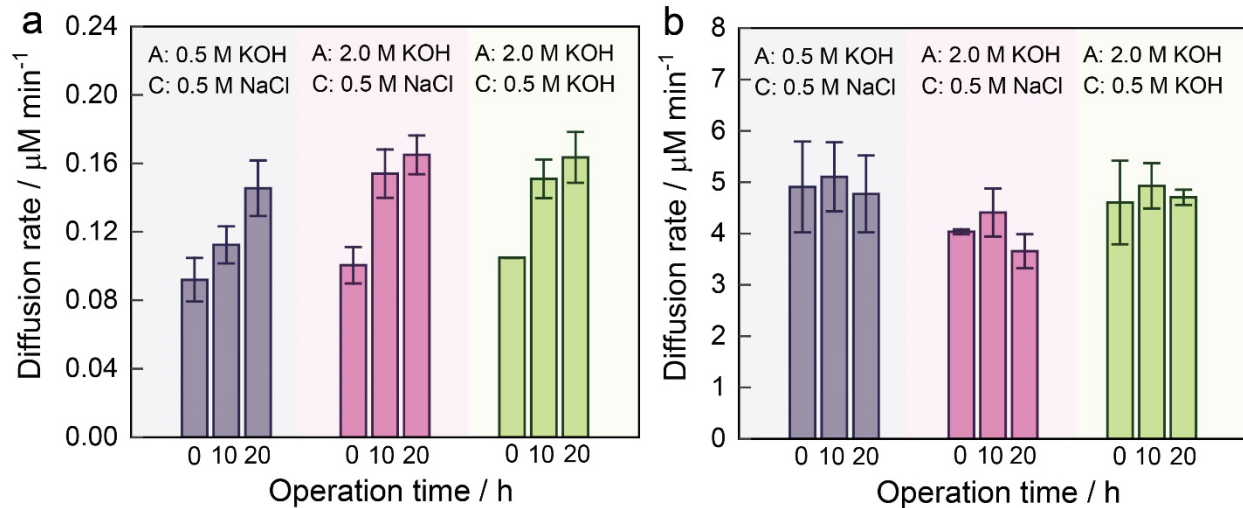
In total water consumption is  $0.0746 \text{ mole}$

$$\text{Volume of water consumption} = \frac{(0.1492 \text{ mol}) (18 \times 10^{-3} \text{ kg mol}^{-1})}{1 \times 10^3 \text{ kg m}^{-3}} = 2.68 \text{ ml}$$

Water volume change ratio =  $\frac{2.68 \text{ ml}}{1000 \text{ ml}} \times 100\% = 0.268 \%$ , so the water volume change due to water splitting is negligible. Therefore, the observed water volume change is not due to the water splitting.



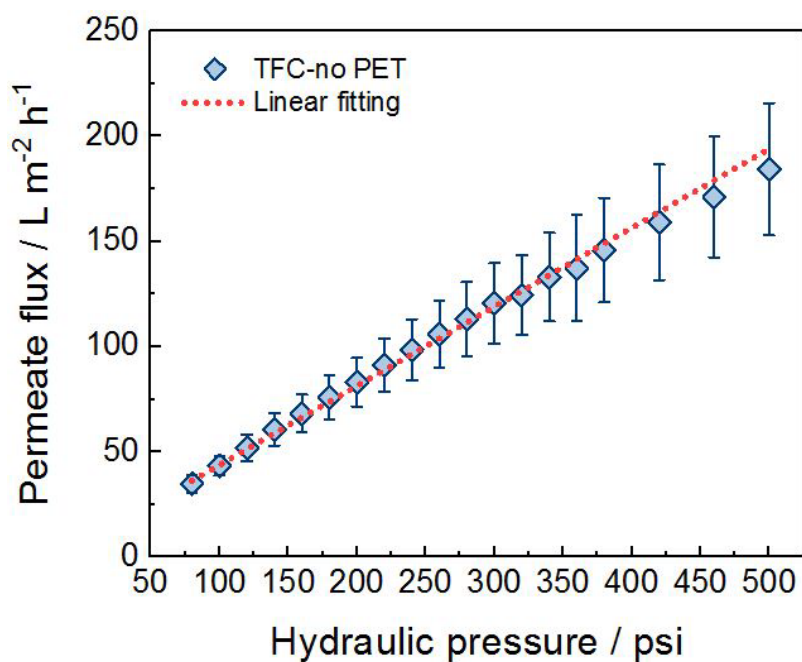
**Figure S8.** Nyquist plot of (a) AEM and (b) TFC-no PET membranes under  $2 \text{ M KOH}$  anolyte condition with a constant current of  $100 \text{ mA/cm}^2$  applied for (1)  $0 \text{ h}$ , (2)  $10 \text{ h}$ , and (3)  $20 \text{ h}$ .



**Figure S9.** Diffusion rate of 0.5 M NaCl into 0.9 M sucrose solution separated by (a) AEM and (b) TFC-no PET membranes after applying a constant current of 100 mA/cm<sup>2</sup> for different operation time in different electrolytes.

**Table S2** Statistical analysis summary of ion diffusion rate of both AEM and TFC-no PET membrane by diffusion conductivity measurement after the electrolyzer performance test under a constant current density of 100 mA/cm<sup>2</sup> for different operation time (0, 10, and 20 h). The slopes, R<sup>2</sup> and *p* values are based on the linear regressions of diffusion rate over time (**Figure S9**).

AEM	0.5 M KOH-0.5 M NaCl	2.0 M KOH-0.5 M NaCl	2.0 M KOH-0.5M KOH
Fitting Slope + SD	0.0028±0.0003	0.0032±0.0012	0.0029±0.0009
R <sup>2</sup>	0.9887	0.8736	0.9011
<i>P</i> value	0.0677	0.2314	0.2036
RO-no PET	0.5 M KOH-0.5 M NaCl	2.0 M KOH-0.5 M NaCl	2.0 M KOH-0.5M KOH
Fitting Slop + SD	-0.0068±0.0154	-0.019±0.0326	0.005±0.0158
R <sup>2</sup>	0.1604	0.2533	0.0911
<i>P</i> value	0.7377	0.6642	0.8048



**Figure S10.** Experimental data for permeate water flux versus hydraulic pressure for TFC-no PET in a dead-end filtration cell with DI water at room temperature.

### References

- (1) Zhou, Z.; Lee, J. Y.; Chung, T.-S. Thin film composite forward-osmosis membranes with enhanced internal osmotic pressure for internal concentration polarization reduction. *Chemical Engineering Journal* **2014**, *249*, 236-245. DOI: <https://doi.org/10.1016/j.cej.2014.03.049>.
- (2) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni - univalent Electrolytes in Water at 25° C. *Journal of Physical and Chemical Reference Data* **1972**, *1* (4), 1047-1100. DOI: 10.1063/1.3253108.