

Supporting Information

**Zeolitic octahedral metal oxide-based membranes for
pervaporative desalination of concentrated brines**

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1. Experimental details

1.1 Synthesis and ion-exchange of ZOMO-CTs

Referring to the method of synthesizing **ZOMO-CT** reported by Zhang et al.,¹ $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (3.97 g, 1.34 mmol) as the W source, SeO_2 (0.284 g, 2.56 mmol) as the Se source, and $\text{C}_4\text{H}_6\text{CoO}_4\cdot 4\text{H}_2\text{O}$ (0.400 g, 1.60 mmol) as the Co source were dissolved in 60 mL of water. The precursor solution for **ZOMO-CT** was obtained. The precursor solution was transferred to a Teflon-lined stainless autoclave and heated in an oven at 100 °C for 24 h. After the autoclave had been cooled to room temperature, the solid was collected by filtration and washed with water for several times and dried.

For ion-exchange procedure, 0.3 g of the as-synthesized **ZOMO-CT** was dispersed in 15 mL of water containing 3.5 wt% salts (i. g. NaCl, CaCl_2 , KCl, $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$, and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) and stirred for 30 min. After the ion-exchanged process, the sample was recovered by filtration and dried.

1.2 Synthesis and ion-exchange of ZOMO-CT-Ms

ZOMO-CT-M was prepared on $\alpha\text{-Al}_2\text{O}_3$ supports (60 mm length, 12 mm outside diameter, 8 mm inside diameter, 34.19 % porosity) by the same hydrothermal method. The precursor solution for the membrane synthesis was prepared by mixing $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ (3.97 g, 1.34 mmol), SeO_2 (0.284 g, 2.56 mmol), and $\text{C}_4\text{H}_6\text{CoO}_4\cdot 4\text{H}_2\text{O}$ (0.400 g, 1.60 mmol). The mixture was transferred to a Teflon-lined stainless autoclave with the $\alpha\text{-Al}_2\text{O}_3$ tube placed vertically and heated in an oven at 100 °C for 24 h. The semi-finished membrane was washed with water for 1 h. The membrane synthesis process was repeated once more with the same procedure. The as-synthesized **ZOMO-CT-M** was washed with water and dried at room temperature.

The ion-exchange process of **ZOMO-CT-M** was carried out by using the pervaporation process. **ZOMO-CT-M** was set in the feed solution (3.5 wt% NaCl, KCl, CaCl_2 , $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, and $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$) to do pervaporation for 30 min. The different ion-exchanged **ZOMO-CT-Ms** were obtained.

1.3 ZOMO-Ca-CT-M regeneration

After using for desalination with 3.5 wt% of NaCl for 15 min, **ZOMO-Ca-CT-M** was regenerated in the feed solution (3.5 wt% CaCl₂) for 30 min by pervaporation. The regenerated membrane was tested again in 3.5 wt% NaCl for 15 min.

1.4 Characterizations

Powder X-ray diffraction (XRD) patterns of the materials and the membranes were obtained on a Bruker, D8 Advance with operating conditions of voltage of 40 KV, current of 40 mA, scan speed of 8 °/min, and 2θ range of 5 – 60°. Elemental compositions were determined by inductive coupling plasma (ICP-AES) method at analysis center of School of Material Science and Chemical Engineering, Ningbo University. Scanning electron microscopy (SEM) and Energy Dispersive X-ray (EDX) observations were carried out on a FEI, Nova Nano SEM 450, operating at 15 kV. Fourier transform infrared spectroscopy (FTIR) was conducted on a Bruker Vertex 70. Water adsorption isotherms were performed on a Micromeritics (3FLEX) apparatus. Prior to measurement, the samples were activated at 80 °C under dynamic vacuum for 2 h.

1.5 Pervaporation measurement

The pervaporation measurement are shown in Figure S5. With a pressure difference between the both sides of the membrane, water was vaporized from the aqueous solution in one side of the membrane and condensed to a cold trap in another side of the membrane.

The flux is calculated by eq. 1, whereas the F , M , A , t represent the membrane flux (kg·m⁻²·h⁻¹), the permeate mass (kg), the membrane area (m²), and the time of desalination (h), respectively.

$$F = \frac{M}{At} \text{ (eq. 1)}$$

The salt rejection is also calculated by eq. 2. In this equation, the $C_{i,F}$ is the concentration of the feed solution, the $C_{i,p}$ means the concentration of the permeate solute, and the R_i represents the salt rejection.

$$R_i = \frac{C_{i,F} - C_{i,p}}{C_{i,F}} \times 100\% \text{ (eq. 2)}$$

To explain the transport of water molecule in pervaporation through **ZOMO-CT-Ms**, the solution-diffusion model was used to determine permeances that were related to the intrinsic properties of **ZOMO-CT-Ms**. Permeance is defined by the driving force normalized flux as eq. 3:

$$J_i = P_i(\alpha_i^f - \alpha_i^p) = P_i(x_i y_i p_i^{sat} - y_i p^p) \quad (\text{eq.3})$$

Where P_i is the permeance of the component i through the membrane, α_i^f and α_i^p are the activity of component i in the feed and permeate; γ_i is the activity coefficient calculated by ENRTL model, p_i^{sat} is the saturated vapor pressure of component calculated by the Antoine equation, p^p is the total pressure on the permeate side, x_i and y_i are the weigh fraction of component i in the feed and permeate, respectively.

In this study, since the permeate side was in an absolute vacuum state, α_i^p was assumed to be 0. Therefore, as noted in eq. 4, permeance was given as:

$$P_i = \frac{J_i}{\alpha_i^f} = \frac{J_i}{x_i y_i p_i^{sat}} \quad (\text{eq. 4})$$

The activation energy for the permeation flux was calculated by the Arrhenius equation, as shown in eq. 5:

$$\frac{d \ln P_i}{dT} = \frac{E_p}{RT^2} \quad (\text{eq. 5})$$

Where E_p , T and R are the apparent activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), the feed temperature (K), and the gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), respectively.

1.6 Computer based simulation

The structures of **ZOMO-CT** with different cation locations and different cation with water were optimized by the DFT calculation using the DMol³ program^{2,3} in the Materials Studio package. The Perdew–Burke–Ernzerhof (PBE) generalized gradient functional and DND basis set were used for calculation.

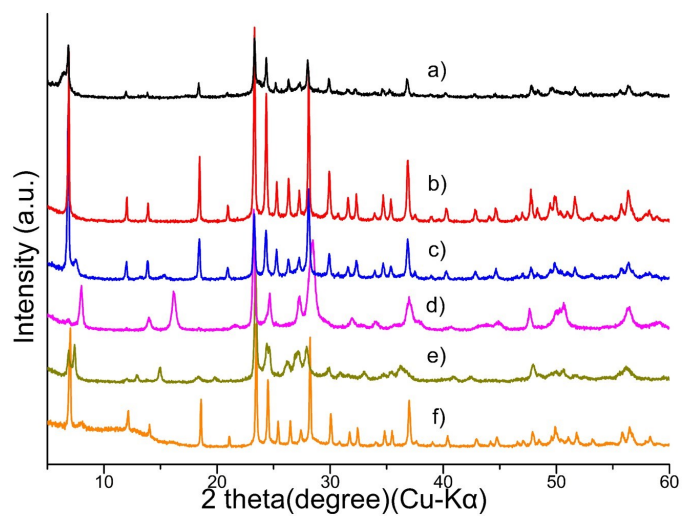


Figure S1. XRD patterns of a) **ZOMO-Al-CT**, b) **ZOMO-Mg-CT**, c) **ZOMO-Ca-CT**, d) **ZOMO-K-CT**, e) **ZOMO-Na-CT**, and f) **ZOMO-CT**.

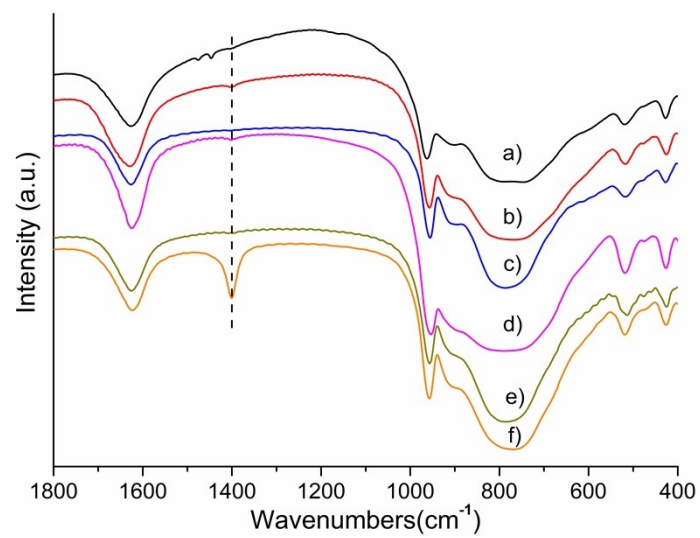


Figure S2. FTIR spectra of a) **ZOMO-Al-CT**, b) **ZOMO-Mg-CT**, c) **ZOMO-Ca-CT**, d) **ZOMO-K-CT**, e) **ZOMO-Na-CT**, and f) **ZOMO-CT**.

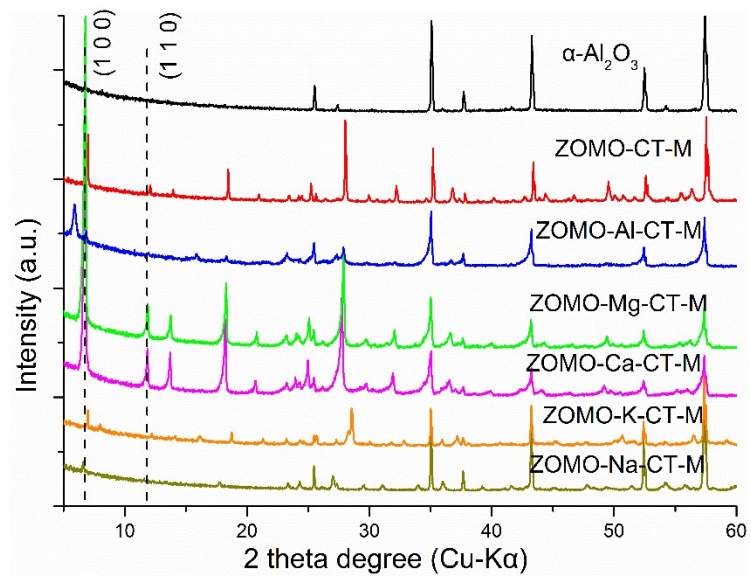


Figure S3. XRD patterns of **ZOMO-CT-Ms**.

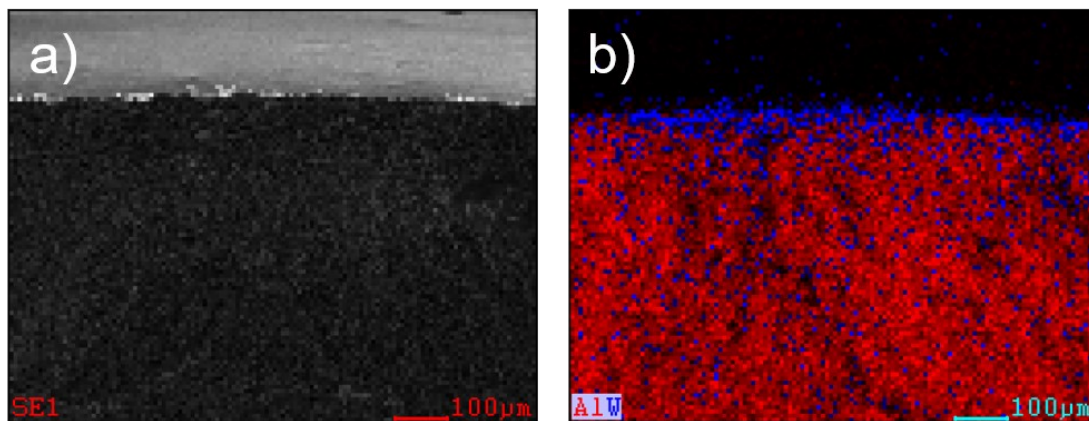


Figure S4. a) SEM image and b) EDX elemental mapping image of **ZOMO-CT** on the α - Al_2O_3 support.

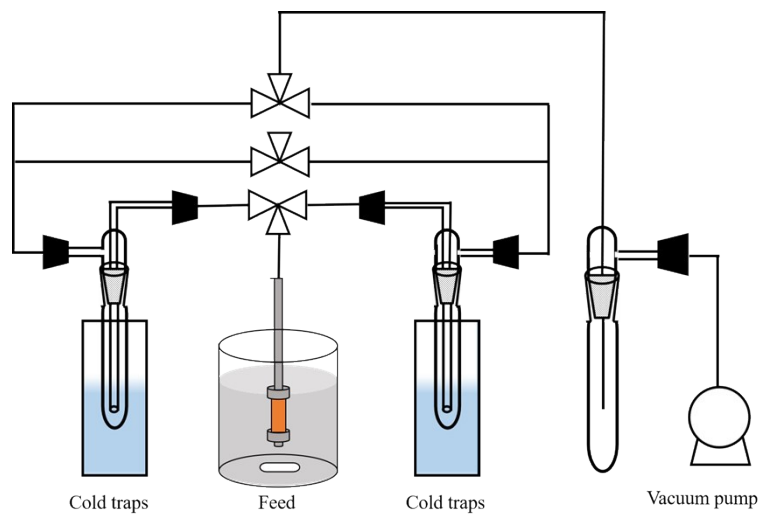


Figure S5. Pervaporation desalination scheme.

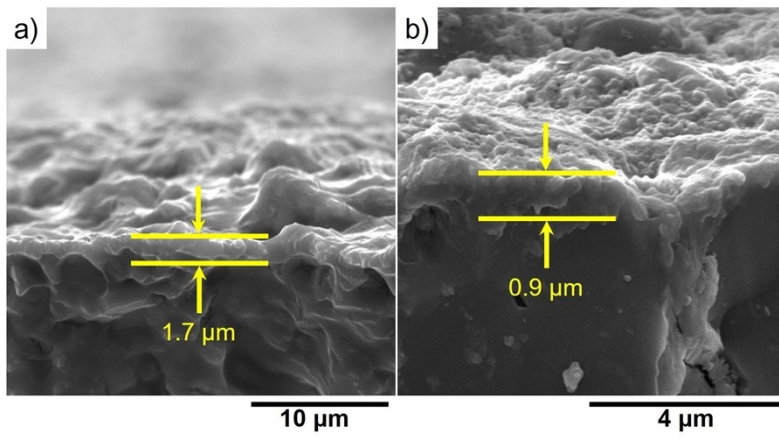


Figure S6. SEM image of the cross section of a) **ZOMO-CT-M** and b) **ZOMO-Al-CT-M**.

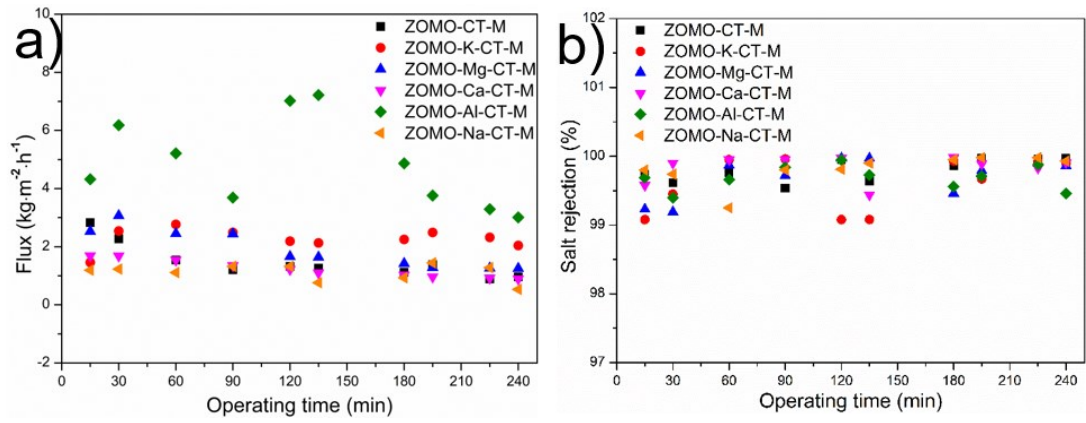


Figure S7. Permeation flux a) and salt rejection b) results of PV desalination as a function of 25 wt% NaCl feed solutions at 25 °C

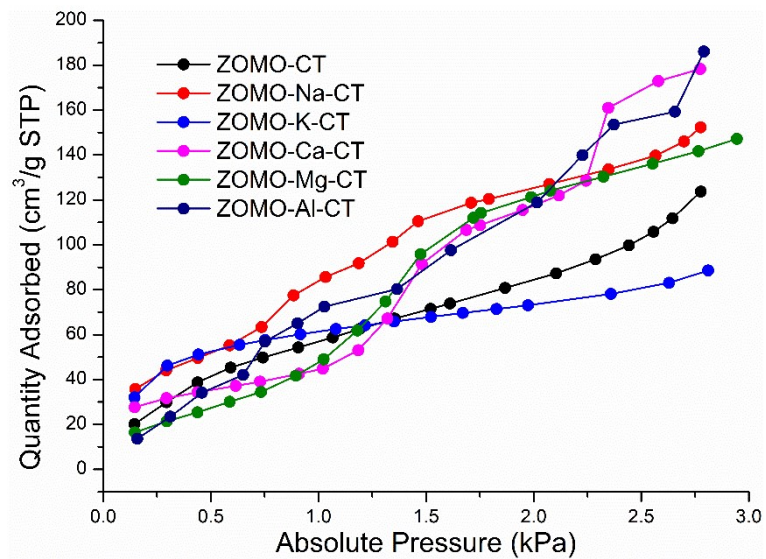


Figure S8. Water adsorption isotherms of ion-exchanged **ZOMO-CTs** at 25 °C.

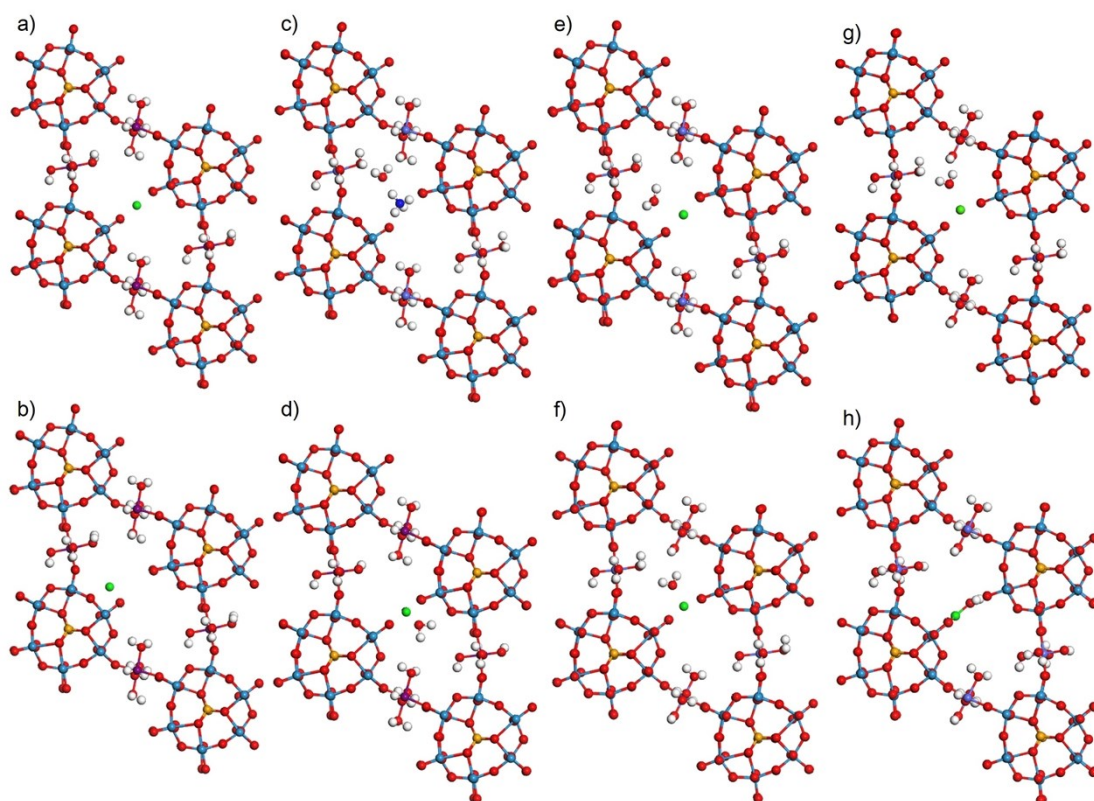


Figure S9. Simulated structures of **ZOMO-CT**, a) cation in A site, $\Delta E = -80.1$ kJ/mol, b) cation in B site, $\Delta E = 0$ kJ/mol, c) adsorbed structure of water in **ZOMO-CT**, d) adsorbed structure of water in **ZOMO-Na-CT**, e) adsorbed structure of water in **ZOMO-K-CT**, f) adsorbed structure of water in **ZOMO-Mg-CT**, g) adsorbed structure of water in **ZOMO-Ca-CT**, and h) adsorbed structure of water in **ZOMO-Al-CT**, W (blue), Se (yellow), Co (purple), O (red), N (deep blue), H (white), cation (green).

Table S1. Summary of present studies on pervaporation desalination by pervaporation

Membrane	T (°C)	Salt rejection	Flux (kg·m ⁻² ·h ⁻¹)	Ref.
Hybrid organic–inorganic membrane	65	99.9%	11.7	4
	25		5.8	
Zeolitic imidazolate framework membranes	50	>99.8%	8.1	5
	75		10.8	
	100		13.5	
Hydrophilic SPEEK/PES composite membrane	70	>99%	6	6
NaA zeolite membrane	69	>99.9%	1.9	7
NaA zeolite membrane on coarse microporous α -Al ₂ O ₃ tubes	75	>99.9%	9.58	8
Zeolite FAU membrane	30	>99.8%	0.96	9
	90		5.64	
UiO-66-NH ₂ membranes	45	>99.7%	1.51	10
	90		2.1	
A novel zeolite 3A incorporated polyether-block-amide composite membrane	40	99.6%	4.57	11
A novel green silica/PVA membrane	60	>99.9%	12.3	12
Graphene oxide-sodium alginate membrane	60	99.41%	8.11	13
Natural zeolite membranes	93	>97.5%	2.5	14
Zeolite-like aluminophosphate membrane	—	>99%	2.14	15
Freestanding self-assembled sulfonated pentablock terpolymer membranes	25	99.5%	3.32	16
La/Y-codoped microporous organosilica membranes	25	100%	10.3	17
This work	65	>99%	13.38	

Table S2. ICP results for fresh and ion-exchanged soft framework

	Co ²⁺	M ^a	NH ₄ ⁺	W	Se
—	1.3	-	0.4	6	1
3.5 wt% AlCl ₃ ·6H ₂ O	0.3	0.8	0	6	1
3.5 wt% MgCl ₂ ·6H ₂ O	1.1	0.4	0	6	1
3.5 wt% CaCl ₂	1.3	0.2	0	6	1
3.5 wt% KCl	0.6	1.8	0	6	1
3.5 wt% NaCl	0.45	2.1	0	6	1

^a M = Na, K, Mg, Ca, or Al

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