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Design of a MXene-Based Ion-Imprinted Membrane for Lithium Ion Recognition

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Apparatus

The morphology characters of materials were observed by field emission scanning electron microscope (SEM, SU-8100, Hitachi, Japan). The roughness of the membrane was observed by Atomic Force Microscope (AFM, AFM 5500, Hitachi, Japan). Thermogravimetric analysis is used to study the thermal stability and composition of substances (TG-DTA, STA 2500 Regulus, NETZSCH, Germany), The hydrophilicity of membranes was investigated by observing water contact angles based on Contact Angle Measuring Instrument (CAMI, KSV CM200, Finland). The lithium ion concentrations were determined by using inductively coupled plasma emission spectroscopy (ICP, VISTA-MPX, Australia). Fourier transform infrared (FTIR) spectra were recorded using a (PerkinElmer FT-IR Spectrum 3) spectrometer with an ATR accessory.Adjustable film applicator (Guangzhou Demanyi Instrument Co., Ltd., range: 0–3500 μm)

Materials

Polyvinylidene fluoride (PVDF, ~500,000 g/mol) was purchased from Arkema, MXene From the MXene Materials Joint Laboratory of Jilin Normal University, bovine serum albumin (BSA, Mn=68000), N, N-dimethylacetamide (DMAC), Tris-HCl buffer solution, dopamine, tetracycline (TC) were purchased from Aladdin. 2-methylol-12-crown-4 (2M12C4), 3-methacryloxypropyltrimethoxysilane (MPTS), ethylene glycol dimethacrylate (EGDMA), olefin Propyl bromide, hydroquinone, sodium carbonate

(Na_2CO_3), sodium hydroxide (NaOH), azobisisobutyronitrile (AIBN) lithium chloride (LiCl), Magnesium chloride ($MgCl_2$), hydrogen peroxide(30%) and methanol were purchased from Sinopharm Group Chemical Reagent. Sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were purchased from Beijing Chemical Works. The experimental water is double distilled water.

Synthesis

4 g of PVDF, 0.1 g of MXene, and 25 mL of DMAc were added to the beaker. Subsequently, a mechanical stirrer was employed to continuously mix the solution at a rotational speed of 155 rpm within a controlled greenhouse environment for 24 h, resulting in a black viscous casting solution. This solution was then allowed to stand undisturbed for 12 h to facilitate the removal of entrapped air bubbles.

A flat-sheet membrane was prepared using an adjustable film applicator. Briefly, 10 mL of the degassed casting solution was transferred onto a clean glass plate using a Pasteur pipette and then spread uniformly with a casting gap of 1 mm. The cast film was exposed to air for 15 s to allow leveling and then immediately immersed in a water bath at room temperature for phase inversion and curing for 24 h. It should be noted that the casting gap of 1 mm refers to the initial wet-film thickness during membrane fabrication, whereas the actual final membrane thickness after phase inversion and curing was measured to be 2.0 ± 0.1 mm ($n = 10$).

Place the aforementioned membrane into a Tris-HCl buffer solution (10 mM, pH 8.5, 50 mL) and allow it to equilibrate for 5 min. Subsequently, introduce 100 mg of dopamine (DA) to initiate the self-polymerization process, resulting in a pDA-coated membrane. Under ambient temperature and continuous mechanical agitation, the reaction is maintained for 6 hours, resulting in the formation of a uniform polydopamine (pDA) coating on the membrane surface. Upon completion of the reaction, thoroughly rinse the membrane with deionized water to remove any unbound polymer and by-products.

Methods

Membrane thickness measurement

The membrane thickness was measured using a thickness gauge after phase inversion and curing. Ten measurements were taken at different positions of the membrane, and the average value was recorded. The final membrane thickness was 2.0

± 0.1 mm (n = 10). This result was consistent with the cross-sectional SEM observation and was used in the revised manuscript to interpret membrane transport resistance, apparent permeation behavior, and the influence of membrane geometry on separation performance.

Determination of specific surface area, pore size distribution and porosity

The specific surface area and pore size distribution of the membranes were determined by nitrogen adsorption-desorption measurements using a surface area and porosity analyzer (Micromeritics ASAP 2460). The samples were degassed under vacuum at 120 C for 6 h prior to measurement. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore volume was derived from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.95. The porosity of the membranes was measured using a gravimetric method. The dry membrane was weighed (mdry), then immersed in ethanol for 24 h, quickly wiped to remove surface liquid, and weighed again (mwet). The porosity (ε) was calculated using the following equation:

$$\varepsilon(\%) = \frac{m_{wet} - m_{dry}}{\rho_{ethanol} * V_{membrane}} \times 100\% \qquad (1)$$

Anti-pollution performance test

The anti-fouling properties of PVDF membranes and MXIM were investigated by BSA adsorption experiments. The PVDF membrane and MXIM were respectively immersed in 10 mL of PBS solution containing BSA at concentrations of 5, 10, 25, and 50 mg L^{-1}, and kept at 4°C for 24 h. The concentrations of BSA in the solution before and after adsorption were measured by UV-Vis, and the adsorption capacity (Q_B, mg g^{-1}) can be calculated according to the following equation:

$$Q_B = \left(C_{B0} - C_B\right) \times \frac{V_B}{m_B} \qquad (2)$$

Here, C_{B0} (mg L^{-1}) and C_B (mg L^{-1}) represent the concentrations of BSA in the solution before and after adsorption, respectively. V_B (L) is the volume of the solution, and m_B (g) is the mass of the membrane.

Swelling degree test

The swelling degree (SD) was calculated using the modified method. The dried membrane was placed in deionized (DI) water for 30 s at room temperature. Then, it was taken out, the surface water was wiped off with filter paper, and the wet membrane (W_1) was weighed immediately. The membrane was then placed in 50 mL of DI water or a 0.05 M single - salt solution (KCl, $AlCl_3$, $CaCl_2$, and $CuCl_2$) for 24 h. Under the same conditions, the weight of the swelled membrane (W_2) was measured. The swelling degree can be calculated according to the following equation:

$$SD = \frac{W_2 - W_1}{W_1} \tag{3}$$

Membrane flux test

Membrane flux is a critical parameter in the practical application of membrane materials. MXIM and the original PVDF membranes were mounted onto a membrane flux testing apparatus with an effective membrane area of 4 cm^2, and the membrane flux was determined under a pressure of 0.15 MPa. The LiCl aqueous solution had a concentration of 20 mg L^{-1}. The membrane flux values for both MXIM and the original PVDF membranes were calculated according to the following equation:

$$J = \frac{V}{S\mathrm{t}} \tag{4}$$

Here, J (mL cm^{-2} min^{-1}) is the membrane flux, V (mL) is the volume of the liquid collected after osmosis, t (min) is the sampling duration, and S (cm^2) is the effective membrane area.

Isothermal adsorption experiment

In the isothermal adsorption study, the PVDF membrane or MXIM was immersed in 10 mL of Li^+ solution with concentrations of 2, 5, 8, 10, 15, 20, 30 and 50 mg L^{-1}, respectively. After adsorption for 3 hours at 25°C, the samples were taken out. The concentrations of Li^+ in the solution before and after adsorption were measured by ICP, and the adsorption capacity (Q_e, mg g^{-1}) was calculated according to the following equation:

$$Q_e = \left(C_0 - C_e\right) \times \frac{V}{m} \tag{5}$$

Here, C_0 (mg L^{-1}) and C_e (mg L^{-1}) represent the concentrations of Li^+ in the solution before and after adsorption, respectively; V (L) is the volume of the solution, and m (g) is the mass of the membrane.The selected concentration range was used to construct the adsorption isotherm and to evaluate the saturation adsorption behavior of the membrane.

Adsorption kinetics experiment

In the kinetic adsorption study, the PVDF membrane or MXIM was immersed in 10 mL of Li^+ solution with a concentration of 20 mg L^{-1} at 25 °C for 5, 10, 15, 30, 60, 90, 120 and 180 min respectively. Then the samples were taken out. The concentration of Li^+ in the solution before and after adsorption was measured by ICP, and the adsorption capacity (Q_t, mg g^{-1}) was calculated according to the following equation:

$$Q_t = \left(C_0 - C_t\right) \times \frac{V}{m} \tag{6}$$

Here, C_0 (mg L^{-1}) and C_t (mg L^{-1}) represent the concentrations of Li^+ in the solution before and after adsorption, respectively; V (L) is the volume of the solution, and m (g) is the mass of the membrane.

Selective adsorption experiment

To further evaluate the membrane response under more complex ionic conditions, selective adsorption experiments were carried out in mixed-ion solutions containing Li^+ and Mg^{2+}, and an extra competing ion such as Ca^{2+} or Al^{3+}. Unless otherwise specified, the initial concentration of each ion was set at 20 mg L^{-1}, and the adsorption experiments were conducted at 25 °C for 60 min. After adsorption, the concentrations of the ions before and after treatment were determined by ICP, and the corresponding adsorption capacities were calculated in the same manner as in the binary system. The competitive adsorption behavior in binary and ternary systems was then compared. The adsorption capacity (Q, mg g^{-1}) was calculated according to following equation, the static distribution coefficient (K, L g^{-1}) , separation factor (α) and the relative separation factor (α') was calculated according to the following equation:

$$K = \frac{Q}{C_e} \tag{7}$$

$$\alpha = \frac{K_{\mathrm{Li}^{+}}}{K_{\mathrm{Mg}^{2+},Ca^{2+},Al^{3+},}} \quad (8)$$

Here, C_e (mg L^{-1}) are the equilibrium concentrations of the target ion

Adsorption-desorption cycle regeneration experiment

Repeatability studies on adsorption and desorption cycle regeneration were conducted in Fig.8c. The same MXIM sample was utilized to evaluate its regeneration performance in Li^+ solution with a concentration of 20 mg L^{-1}. Once adsorption reached equilibrium, the Li^+ loaded on the saturated MXIM were eluted using 0.5 mol L^{-1} hydrochloric acid solution, after which the MXIM was reused in subsequent adsorption-desorption cycles. To assess the regeneration capability of MXIM, the adsorption-desorption cycle was repeated ten times.

Static selective permeability experiment

The static selective permeation experiment was further extended to a ternary system. The membrane was placed in the center of a customized H-type diffusion device. The feed compartment contained 100 mL of mixed-ion solution. For the binary system, the solution contained Li^+ and Mg^{2+}. For the ternary system, the solution contained Li^+, Mg^{2+}, and Al^{3+}, each at 20 mg L^{-1}, and the receiving compartment contained 100 mL of deionized water. Samples were taken from the receiving side at predetermined time intervals and analyzed by ICP to evaluate the competitive ion transport behavior under binary and ternary conditions. Calculate the permeation flux (J, mg min^{-1} cm^{-2}), calculate the permeability coefficient (P, L min^{-1} cm^{-1}) and calculate the permeation selectivity coefficient (β) according to the following equation:

$$J = \frac{\Delta C_{\mathrm{R}} V_{\mathrm{R}}}{\Delta \mathrm{tA}} \quad (10)$$

$$P = \frac{Jd}{C_{\mathrm{F}} - C_{\mathrm{R}}} \quad (11)$$

$$\beta = \frac{P_{\mathrm{Mg}^{2+}}}{P_{\mathrm{Li}^{+}}} \quad (12)$$

Photocatalytic degradation performance test

To evaluate the practical application performance of the prepared membrane materials, tetracycline was selected as a representative to study its removal performance. A piece (4 cm^2) of PVDF membrane or MXIM was immersed in 50 mL of tetracycline (TC) solution with a concentration of 10 mg L^{-1}. To ensure adsorption equilibrium, it was stirred in the dark for 30 minutes first. Then, the photocatalytic degradation reaction was initiated under visible light excitation (using a 300-watt xenon lamp, $\lambda \geq 420$ nm), and samples were taken every 30 minutes. The concentration of TC was determined by high-performance liquid chromatography - ultraviolet detection (HPLC-UV).