Fabrication of highly selective ion imprinted macroporous membranes with crown ether for targeted separation of lithium ion

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ABSTRACT

A macroporous polymer- ion imprinted macroporous membranes (IIMMs) was synthesized using Poly (vinylidene fluoride) (PVDF) as membrane matrix and crown ether (CE) as function monomer by using phase inversion technique. In addition, dopamine (DA) was introduced between PVDF membrane matrix and imprinted layer to ensure combinative in a stable fashion. Attributing to the unique properties of CE can react with alkali metal ions to form a stable complex, promoting the growth of large and homogeneous specific recognition cavity on the surface of IIMMs, hence the IIMMs exhibited highly effective in separation performance of template ion (Li$^+$). Classical adsorption isotherms including Langmuir and Freundlich and kinetic toward Li$^+$of IIMMs and NIMMs were employed to describe the adsorption equilibria. The excellent separation (maximum selectivity factor α is 4.42) and recognition behavior coupling with the low preparation consumed and green, quick, facile synthesis conditions make the as-prepared IIMMs attractive in broad technological applications of recognition and separation of Li$^+$in salt lake.

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1. Introduction

Lithium resource, which is widely used in the aluminum production, metallurgy, pharmaceuticals industry and Li ion (Li$^+$) battery industries [1–3] as one of the rare elements on the earth. Recently, the existing lithium resources are sharply depleted as the market grows. Therefore, researchers pay more attention to develop the separation and concentration of Li$^+$. Importantly, on account of the salt lake brine [4,5] in a high molar rate of Mg^{2+}/Li$^+$, development of selective separation of Li$^+$ from similar compounds and complex is necessary.

Macroporous polymer is an emerging class of fascinating porous materials for separation and purification field [6–8]. Typically, macroporous membranes material as adsorbents are widely used in many separation process due to low energy consumption, simple preparation methods, environmental protection and superior industrial application [9–11]. It has also caused great repercussions not only in wastewater treatment, but also in the resource concentration [12,13]. However, the macroporous membranes still suffer from lack of selectivity due to their limited specific binding, this is the most challenge task for further development. Hence, increasing

selectivity of macroporous membranes for specific target substance is urgently needed. As the specific recognition and separation materials, molecularly imprinted polymers (MIPs) are preferred, which play central roles in bioseparation, targeted therapy, and membrane separations [14–18].

Similar to MIPs, ion imprinted polymers (IIPs) have received much attention [19,20]. IIPs refer to functional monomers, template ion and cross-linkers interaction. Subsequently, the template ion is extracted without damaging the structure to obtain a gap as same as the size of target ion. It has also caused great applications not only in recovery of alkali metals, but also in heavy metals and rare earth metal [21–23]. At present, a number of works concerning IIPs have been conducted. For instance, Meng et al. investigated IIPs to specifically recognize Cerium, exhibited high selectivity and satisfactory adsorption capacity toward Cerium [24]. Maryam Fayazi et al. used magnetic IIPs nanoparticles for the sensitive and selective detection of Pb (II) ions by graphite furnace atomic absorption spectrometry [25]. Despite decades of intense research in IIPs, it is still a issue to engineer and synthesize a straightforward material with high regeneration and excellent permselectivity to template ion.

As high selectivity for metal ions and the complexes with metal ions are more stable, crown ethers (CEs) have caused worldwide concern during the past years. CEs are very useful model compounds that possess a variety of chemical structures and also designed as functional monomers for the preparation of IIPs.

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According to the previously reported, due to the similar size, 12-crown-4 can easily combine with Li$^+$ forming a stable complex [26,27]. Considering the above-mentioned attractive properties of CEs in the preparation of IIPs, a breakthrough strategy of CEs as function monomer was engineered in this work.

Ion imprinted macroporous membranes (IIMMs) refer to graft IIPs at the surface of macroporous membranes, which combine the outstanding advantages of macroporous membrane material and IIPs provide the membranes with specific selectivity toward template ions, easily regenerated process and low energy consumption. Importantly, IIMMs could offer artificial specific recognition cavities on the surface of macroporous membrane, so that improving the affinity between IIMMs and template ions. These recognition cavities can identify template ions among other ions coexisting in the solution, and they are not suitable for competitive ions. Therefore, the IIMMs could possess a high adsorption selectivity and specificity toward template ions.

Poly(vinylidene fluoride) (PVDF) as an excellent membrane material has been widely used for preparing superhydrophobic membranes, which possessing outstanding properties such as good thermal stability, high mechanical strength and relatively low cost [28–30]. However, it is a general issue that imprinted layer cannot combine in a stable fashion with PVDF macroporous membranes matrix. At present, a large number of reports about dopamine (DA) as an excellent surface-adherent material, which can polymerize onto all kinds of inorganic and organic surfaces to form a heterogeneous polydopamine (PDA) thin layer [31–33]. Attributed to this breakthrough study, PDA thin layers can take place a stabilized cross-linked interaction between imprinted layer and PVDF macroporous membrane matrix, so that, nearly all the imprinted cavities are accessible to template ion and more stable structure could be obtained.

Here, the PVDF macroporous membranes matrix were synthesized by phase inversion method, and CEs were selected with template Li$^+$ to form a stable complex as IIPs. As evidenced in this study, these IIMMs with CEs as function can not only largely improve the adsorption capacity, but also reinforce the chemical stability and regeneration. That is to say, the IIMMs could work very well for selective separation and purification of Li$^+$ in a complex system. In practice, the IIMMs prepared in this way have the advantages of straightforward and environment-friendly processes, directing it as a promising candidate for widespread application of recognition and separation of Li$^+$ in salt lake.

2. Experiment

2.1. Materials

Poly (vinylidene fluoride) (PVDF) powder was purchased from French company Arkema. N,N-dimethyl acetamide (DMAc, 98%, Aladdin), polyvinylpyrrolidone K30 (PVP, molecular weight 40,000, Aladdin), Tris (hydroxymethyl) aminomethane (Tris–HCl, 99%, Aladdin), dopamine (DA, 98%, Aladdin), 30% potassium hydride dispersion in mineral oil (KH, 98%, Alfa), 2-methylol-12-crown-4 (2M12C4, 98%, Aladdin), lithium chloride (LiCl, Aladdin), magnesium chloride (MgCl$_2$, Aladdin), N, N- dimethyl formamide (DMF, 98% Aladdin), allyl bromide (98% Aladdin), dichloromethane (98%, Aladdin), ethylene glycol dimethacrylate (EGDMA, 98%, Aladdin), azo-bis-isobutyronitrile (AIBN, 99%, Aladdin) were used as received. Doubly distilled water was used in all cleaning processes and aqueous solutions.

2.2. Characterization

Nuclear magnetic resonance spectroscopy (NMR) spectra were recorded at room temperature on a Varian Mercury-400 spectrometer. The Attenuated total reflection-fourier transform infrared (ATR-FTIR) spectra (4000–800 cm^{-1}) for different PVDF membranes were recorded on a FT-IR Nicolet 560 apparatus (U.S.A.), and ZnSe was used as the crystal plate. The prepared macroporous membranes were examined by scanning electron microscopy (SEM, S-4800). Atomic adsorption (AA, TAS-986) was used to measure the metal ion concentration.

2.3. Synthesis of Functional monomer 2-(allyloxy)methyl-12-crown-4 (2AM12C4)

Firstly, 0.32 g KH, 0.4 g 2M12C4 and 30 mL DMF were mixed in a 100 mL flask, stirring at room temperature for 30 min, and then 1.22 g allyl bromide was added. The mixture was stirred overnight. The reaction was quenched with methanol, and then the methanol was removed by a rotary evaporator at 45 °C for several times. After that, the product was extracted with dichloromethane and washed with water for three times, dried with Na$_2$SO$_4$(s) and filtered. Finally, the product was dealt with rotary evaporator to remove the redundant DMF. These results demonstrate that the product is 2AM12C4.

2.4. Synthesis of pristine PVDF microporous membrane and PDA thin layer on PVDF microporous membrane

4 g PVDF powder, 20 mL DMAc and 20 mg PVP were mixed into a three-neck round-bottomed flask to obtain the casting solution of pristine PVDF macroporous membrane. The mixture was mechanically stirred for 12 h at 30 °C and stored for another 24 h at 30 °C to remove the air bubbles. Sequentially, the casting solution was spread on a undefiled glass plate using a doctor knife, and then immersed into deionized water. The phase inversion process taken place between casting solution and the deionized water. After that, the pristine PVDF macroporous membranes were stored in deionized water before use.

In a typical dopamine modified PVDF macroporous membrane synthesis, first, one piece of pristine PVDF microporous membrane (40 mm in diameter, 0.10 g) was dipped into 50 mL 10 mM Tris-HCl (pH = 8.5) aqueous solution for 5 min. Second, 100 mg of DA was added to above solution to start the self-polymerization reaction. The self-polymerization process was lasting for 6 h under persistently mechanically oscillation at room temperature, and then the PDA thin layers could be achieved on the macroporous membrane surfaces. Finally, the PDA@PVDF macroporous membrane was obtained after being rinsed with deionized water to wash out redundant PDA particles and unreacted dopamine.

2.5. Preparation of ion imprinted macroporous membranes (IIMMs)

The IIMMs prepared procedure of PDA@PVDF was conducted by surface-imprinted polymerization. 1.23 g 2AM12C4, 0.302 g LiCl and 60 mL methanol were added into a round-bottomed flask. The reaction mixture was sealed and stirred in a water bath at 25 °C for 2 h for the self-assembly of the 2AM12C4 and Li$^+$. Sequentially, 0.1 mL EGDMA, 0.01 g AIBN and one piece of PDA@PVDF (40 mm in diameter, 0.14 g) macroporous membrane were added into above solution. The imprinting procedure was carried out in the protection of nitrogen condition. The mixture was subject to reflux at 60 °C overnight with continuous stirring. Following this polymerization procedure, the IIMMs should be extracted by 0.5 mol/L hydrochloric acid to remove the Li$^+$. After drying, the IIMMs were obtained. As the control, the non-imprinted macroporous membranes (NIMMs) were prepared without the addition of template ion and subjected to the same procedure.