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Hydrophilic nanoporous ion-exchange membranes as a stabilizing barrier for liquid–liquid membrane extraction of lithium ions

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ABSTRACT

Stability of supported liquid membrane (SLM) has been a key issue in the application of high efficiency liquid membranes. In this paper, a nanoporous ion exchange membrane, prepared by blending polyethersulfone (PES) with sulfonated poly (phenyl ether ketone, SPPESK), was utilized as the stabilizing barrier for the extraction of lithium ion based on liquid–liquid membrane extraction. The membrane was prepared via immersion precipitation and the ratio between PES and SPPESK was varied in order to obtain a membrane with the best performance. It was found that at a PES/SPPESK ratio of 6/4 and a polymer concentration of 30 wt%, the membrane showed a Li^+ flux of 1.67×10^{-8} mol cm^{-2} s^{-1} at a Li^+ feed concentration of 0.13 mol/L. The membrane demonstrated nearly unchanged stress but a slight decline in elongation after 50 days in contact with the organic extractant, indicating the potential solvent resistance. Using tributylphosphate (TBP) as the extractant and kerosene as the diluent, lithium extraction and stripping were demonstrated in both single-staged and sandwiched membrane extraction contactor systems. The preliminary results on using SPPESK/PES barrier membrane for stabilizing the liquid membrane will lead to a new scientific and technology development in lithium mining from brine and seawater in the near future.

1. Introduction

Lithium is a rare element on earth, which has important applications in many fields including portable power sources, refrigerants, ceramics, and medicines. With the depletion of fossil fuel and growing energy demand, the demand for lithium is expected to expand [1]. The two major sources for Li are Li-containing minerals (spodumene, petalite and lepidolite) and subsurface brines [2]. In china, the total lithium reserve is 0.54 million tons, where over 80% is present in the subsurface brines. However, the presence of high concentration of interfering ions including Mg, Na, and K has been a major obstacle for the highly efficient, environmental friendly extraction of lithium.

Depending on the composition of the brine water, many approaches have been developed for lithium extraction including chemical precipitation [3,4], ion exchange [5,6], calcination leaching [7,8], carbonization [9,10], and electrodialysis [11,12]. However, these methods are technically difficult for the brine sources in China and economically unfavorable. In northwest China, there are natural salt lake brine resources containing high concentration of lithium ions, ranging from a few hundred ppm to 7000 ppm. Although highly concentrated in lithium, the purification of lithium from the brine is very difficult due to a very high concentration of magnesium. In general, the ratio of Mg^{2+}/Li^+ is larger than 40 and to some extreme cases, the ratio is more than 200 [7,8,10]. At such a high salinity and high Mg^{2+}/Li^+ ratio, above technologies are not viable. Nanofiltration processes [13] have been investigated as the potential technologies for the extraction of lithium from the salt lake brine, but failed due to the precipitation of salt in the membrane module. Solvent extraction [14] and more advanced supported liquid membranes (SLMs) [15,16] are more attractive for the lithium extraction because of the high efficiency and more importantly the higher selectivity. Besides, SLM is characterized by low energy consumption and small footprint.

Separation in a SLM is achieved through affinity binding and/or complexation of the liquid membrane with a particular chemical species [17]. The membrane functions as a support to hold the chemical extractant and the diluent. Ma et al. [15] reported the extraction of lithium from brine sources such as geothermal water and seawater based on SLM. A carrier combination of LIX54 (main component is α-acetyl-m-dodecylacetophenone) and TOPO (tri-octyl

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phosphine oxide) had a synergistic effect for lithium extraction and the optimal extraction efficiency of the system was higher than 95% for a model feed solution containing Na^+, K^+, and Li^+ at pH greater than 12.5. Although no stability results were reported yet, loss of organic extractant and swelling of the membrane support would eventually lead to instable operation. Ideally, the membrane should be stable against the solvent and keep the liquid membrane from leaching out. However, loss of liquid membrane and stability of the membrane materials have been the key issues hampering the application of SLMs [17–20].

Efforts have been focused on preventing the loss of organic liquid extractant including the application of gelating coating layer [19,21], interfacial polymerization coating [17], ion exchange membranes [22], immobilization of extraction molecules to the membrane matrix [23–25] and composite membrane with hydrophilic and hydrophobic layers [26–29], addition of extractant into the strip solution [30], and optimization of the membrane module structure [31]. These membranes have shown some advantages but performance stability was still below satisfaction. By applying composite hollow fiber membranes consisting of a polyelectrolyte coating (sulfonated polyether ether ketone (SPEEK)) and a polysulfone or polypropylene support, a stable performance over 3 months demonstrated that the loss of organic liquid phase was effectively prevented [20]. Careful examination revealed that the polysulfone (PSf) and polypropylene (PP) support became brittle, caused by the attack of the organic extractant, but the SPEEK layer appeared to be stable. The main difference of the two materials is that SPEEK is intrinsically hydrophilic and PSf and PP materials are hydrophobic.

SPEEK layer acted as a barrier to prevent the loss of organic solvent while allowed free diffusion of cations. The mechanical strength of SPEEK in aqueous phase is low. It is envisioned that blending of SPEEK with other hydrophobic polymers may effectively improve the membrane hydrophilicity and solvent resistance, allowing the free passage of ions as well. In a liquid–liquid membrane contactor system [20,32], the mechanically strengthened membrane absorbs water due to hydrophilic sulfonated polymer, but not organic solvent. Thus, the damage of the organic solvent to the membrane polymer will be significantly low and long term stability in the membrane material is expected. This strategy of applying a hydrophilic blend membrane as a stabilizing membrane in a membrane contactor has not yet been reported in literature.

This paper reports the novel application of a blend membrane consisting of SPPESK blend with a hydrophobic polyethersulfone polymer in a membrane contactor system for extraction of lithium from a high salinity brine solution. By increasing the concentration of the SPPESK, the hydrophilicity and water uptake of the membranes were correlated to the stabilization of the membrane and ion transport properties. The performance of the resulting membrane was systematically investigated for the extraction of lithium ions from a synthetic salt lake brine with a large amount of magnesium. A continuous extracting/stripping process is demonstrated using a sandwiched membrane contactor configuration.

2. Mechanism of lithium extraction in membrane extraction

Membrane extraction is a process combining membrane and organic extractant. The use of tributylphosphate (TBP) as the extractant for lithium has been established in 1970s by Joseph et al. [14]. As shown in Scheme 1, TBP, together with $FeCl_3$ as a co-extractant, is a selective extractant for lithium. $FeCl_3$ can form complex with Cl^-, resulting in $FeCl_4^-$. $FeCl_4^-$ then reacts with Li ions to form $LiFeCl_4$. TBP coordinates with $LiFeCl_4$ at a molar ratio of 2:1 and thus extract lithium from aqueous phase to the organic phase. In the stripping process, the $LiFeCl_4 \cdot 2TBP$ complex reacts with hydrochloride and release lithium ions into the acid. The formation of the $LiFeCl_4$ is essential for the accomplishment of the extraction process since a direct reaction between TBP and LiCl is not possible. Therefore, $FeCl_3$ is added into the feed solution at a ratio of $FeCl_3$:LiCl not less than 1:1. As shown in Scheme 1 (the fourth reaction), the extraction of $FeCl_3$ is possible when the aqueous phase is a strong acid. Therefore, the pH of the feed solution is of potential importance for the extraction of lithium together with $FeCl_3$. By using highly concentrated hydrochloride solution (i.e. 4 M HCl), Fe remains in the organic phase and lithium ion is stripped into acid. In this way, lithium is selectively extracted from a mixture of brine solution.

$$FeCl_3 + Cl^- \Leftrightarrow FeCl_4^-$$
$$Li^+ + FeCl_4^- \Leftrightarrow LiFeCl_4$$
$$LiFeCl_4 + 2TBP_{(O)} \Leftrightarrow LiFeCl_4 \cdot 2TBP_{(O)}$$
$$LiFeCl_4 \cdot 2TBP_{(O)} + HCl \Leftrightarrow HFeCl_4 \cdot 2TBP_{(O)} + LiCl$$

Scheme 1. The extraction of lithium using TBP as the extractant.

In this work, a membrane permeable for cations is utilized as a barrier for the organic extractant. Therefore, an extra diffusion transportation step exists in the membrane contactor system, as shown in Fig. 1 and listed in the following:

1) Diffusion of $LiFeCl_4$ from the bulk feed to the membrane/aqueous interface;
2) Diffusion of $LiFeCl_4$ from the feed/membrane interface to the membrane/organic extractant interface; upon contact, the concentration gradient is the driving force; this step is an extra step in the new membrane contactor system due to addition of the barrier layer to the organic extractant;
3) The ion complex reacts with TBP, forming an extracting complex at the membrane/extractant interface;
4) The extracting complexes diffuse into the bulk phase of the organic extractant. The driving force is the concentration gradient of the organo–ionic complex.

In the stripping process, reversed steps could be easily identified, thus not listed here. Based on the authors knowledge, there were no open publications yet on the using membrane contactor for extraction of lithium based on the above extraction mechanism. We believe that our work on using blended SPPESK/PES membrane as a barrier for stabilizing the liquid membrane for extracting lithium from a brine solution is unique and the first ever in the open literature.

3. Experimental

3.1. Chemicals and materials.

Polyethersufone (PES Ultrason E6020P) was kindly supplied by BASF and was dried one week at 90 °C before usage. Sulfonated polyphenyl ether sulfone ketone (SPPESK) was supplied by Dalian Polymer Co. Ltd. (Dalian, China PNM P0403-029) [33]. Dimethylacetamide (DMAc), and tributyl phosphate (TBP) were obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Kerosene was used as diluent for organic extractant (Petrochemical Corporation, China). Lithium chloride (anhydrous, Analytic grade) and hydrochloric acid (36–38%) were provided by Nanjing Chemical Reagent Co. Ltd. (Nanjing, China). All chemicals were of chemical grade and used without further purification. Deionized water was used throughout the experiments.