博　士　論　文　の　内　容　の　要　旨

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論文題目	Study on carbon nanomaterials modified NF membrane and Mg^{2+}/Li^{+} separation performance （カーボンナノ材料修飾 NF 膜とその Mg^{2+}/Li^{+}分離性能に関する研究）

（博士論文の内容の要旨）

The rapid developments of electric-energy storage technology, especially in the application of electric vehicles, have promoted an increasing demand for lithium resources. Owing to the low cost and large lithium reserves, lithium recovery from salt-lake brines has become a growing trend in the lithium recovery industry. Effectively separate Li^{+} and the co-exist Mg^{2+} is critical for enriching and extracting high purity lithium products from salt-lake brines. Nanofiltration (NF) technology is promising for separating Mg^{2+} and Li^{+} in salt-lake brines. Till now, it is still challenging to obtain both high separation ability and high flux at the same time, which is the bottleneck of the industrial application of NF membrane for lithium extraction. For industrial applications, an optimization of the membrane structure and chemical composition is necessary to ensure highly selective separation, anti-pollution, and long-term stable performance. In this work, we adopted several carbon materials to improve the Mg^{2+}/Li^{+} separation performance and efficiency of NF membranes, and comprehensively discussed the results and mechanism of the resulted carbon-based NF membranes from the perspectives of multiple aspects. Based on the above research process, the main research contents of this paper are as follows:

(1) A novel NF membrane was optimized by doping graphene oxide (GO) additives into the ultrafiltration (UF) base membrane. The effects of GO doping content on the morphology, structure and surface properties of UF membrane and the final NF membrane were studied comprehensively. The hydrophilic GO acted as a “bridge” between UF membrane and polyamide layer due to the “anchor effect”, which significantly enhanced the interaction between base membrane and polyamide layer. The results revealed that with ultra-low GO doping content of 0.05 wt%, the final NF membrane exhibited a high selective separation capacity for Mg^{2+} and Li^{+}, and the flux increased by about 119% compared with the pure NF membrane without GO. Additionally, due to the high stability of membrane, the excellent separation capacity of modified NF membrane only changed slightly after 7-day cycle filtration test. Importantly, a small amount of GO doping greatly improved the permeability of both UF and NF membranes, which correspondingly improved the separation efficiency and accelerated the filtration rate. (2) We developed another novel NF membrane by incorporating nano-sized aminated graphene quantum dots ($GQDs\text{-}NH_2$). The effect of $GQDs\text{-}NH_2$ dosage on the structure and properties of the NF membrane was systematically investigated by several characterization methods. The modified NF membrane with optimized $GQDs\text{-}NH_2$

incorporation of 0.03 wt% exhibited a higher positive chargeability, a high separation ability and a higher difference of up to 77% between Mg^{2+} and Li^{+} rejection, suggesting its excellent Mg^{2+}/Li^{+} separation capability. Importantly, the modified NF membrane had a high permeation flux of 11.94 L/m^{2}hbar, which was 137.8 % more than that of pure NF membrane with no GQDs-NH_2. Furthermore, the (GQDs-NH_2)-optimized morphology structure and hydrophilicity led to strong anti-fouling and stability of the final NF composite membrane.

(3) We successfully synthesized a new functional nano-additive called potassium carboxylate functionalized multi-wall carbon nanotubes (MWCNTs-COOK) and introduced it into the interfacial polymerization system to fine-tune the structure and properties of the NF membrane. The embedded MWCNTs-COOK (150ppm) tightened the network-crosslink structure of the selective layer and contributed to a dense hydrophilic membrane surface with high positive chargeability. In addition, MWCNTs-COOK nano-additives in membrane created some intrinsic fast transport channels for water molecules. The MWCNTs-COOK (150ppm)-assisted NF membrane exhibited a remarkable high flux of 12.23 L/m^{2}hbar, a high separation ability, and a high difference in Li^{+} and Mg^{2+} rejections around 77%, indicating an excellent Li^{+} enrichment and Mg^{2+} removal capabilities, and breaking through the trad-off limit of permeate flux. Simultaneously, the comprehensive performance of the NF membrane can be maintained stably even in long-term utilization.

(4) Herein, we proposed another (MWCNTs-COOK)-engineered substrate membrane to regulate the NF membrane for fast and efficient separation of Li^{+} and co-existing Mg^{2+} in brines. Results proved that the fixed MWCNTs-COOK strengthened the connection between the substrate and the formed polyamide layer, and it endowed both the substrate and the final NF membrane with higher water permeability. The membrane performance characterization indicated that with a low MWCNTs-COOK content of 0.012 wt% in the NF membrane, the difference between rejections of Mg^{2+} and Li^{+} reached up to 86.94 %. Note that the modified NF membrane showed a high flux of high flux of 11.46 (L/m^{2}hbar), which was 2.28 times as high as that of the NF membrane without MWCNTs-COOK. Moreover, the NF membrane also performed stable during the long-time filtration due to the improved structure and hydrophilicity of membrane.

In summary, the incorporation of carbon nanomaterials is an effective way to improve the Mg^{2+}/Li^{+} separation efficiency of NF membrane. This work opens a simple and effective pathway for accelerating Li^{+} enrichment and Mg^{2+} removal, which has great potential for lithium extraction application from salt-lake brines that loaded with high concentration of Mg^{2+}.