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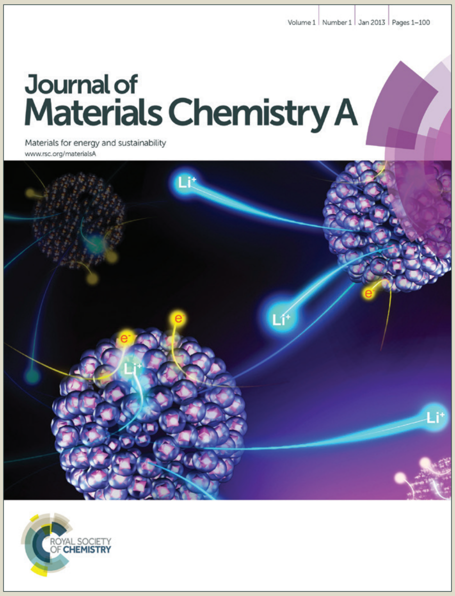

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Effective Recovery of Acids from Iron-Based Electrolytes Using Graphene Oxide Membrane Filters

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The efficient recovery of acids from iron-based electrolytes using graphene oxide (GO) membranes was demonstrated for the first time. The results revealed that the amount of H^+ permeating the GO membranes and reaching the drains was two orders of magnitude larger than that of Fe^{3+}. Notably, when the $FeCl_3$ source concentration was reduced to certain extent, Fe^{3+} could be completely blocked by GO membranes. The mechanism for the effective separation of H^+ from Fe^{3+} was studied, suggesting that the molecular sieving effect of GO nanocapillaries and the coordination between Fe^{3+} and GO were responsible for the effective blockage of Fe^{3+} while the rapid propagation of H^+ through the hydrogen-bonding networks along the water layers within the interlayer spacing was responsible for the fast migration of H^+. These properties made GO membranes promising as cation-exchange membranes for the applications of waste water reuse and membrane separation.

A huge amount of waste water containing acids and mixed metallic salts has been produced by steel and electroplating industries in processes such as pickling, passivating, cleaning and rinsing, which has caused serious hazards to ecological systems.[1] So far, several methods have been developed for the treatment of such waste pickle liquors including direct neutralization, pyrohydrolysis, distillation[2], solvent extraction[3], ion exchange technique[4-6], electrodialysis[7,8] and diffusion dialysis[9-11]. Among them, diffusion dialysis with anion-exchange membranes is attractive for the recovery of acids from mixed salts due to the advantages of energy saving and ease of operation. With anion-exchange membranes, the anions in spent pickling solutions are attracted by the positively charged ions fixed in membranes while the metallic cations are strongly repulsed. Exceptionally, the hydrated protons possess relative high mobilities in the membranes due to their small sizes and charges. However, in spite of these advantages, the protons in anion-exchange membranes are more or less repulsed by the fixed ions with positive charges, which will degrade the capability of acid recovery using anion-exchange membranes. For example, in most cases of diffusion dialysis with anion-exchange membranes, the recovery of acids was around 80% and the Fe leakage was around 10%~20%,[12,13] which has not reached the standard for producing acids with high quality. In addition, the typical polymer-based ion exchange membranes are usually thick and dense, which makes them not suitable for large-scale industrial applications. Thus far, the diffusion dialysis with anion-exchange membranes for collecting acids from waste pickle liquors has not been used on a large commercial scale due to the high costs and poor performance of the existing membranes. Scientists are now searching for a new kind of light material with excellent proton transport property and effective capture of heavy metal ions simultaneously.

Among the existing materials, graphene oxide (GO), prepared by oxidation and exfoliation of graphite,[14,15] has been demonstrated to be a promising barrier film which exhibits excellent selectivity towards various gases[16] and liquids[17-20]. In a piece of GO sheet, oxygen-containing functional groups tend to cluster on the 2D matrix, resulting in sp^2 regions decorated randomly on the sp^3 C-O matrix.[21,22] This unique structure facilitates diverse interactions with ions in solutions, which endows GO sheets with selectivity towards different ions[18,19]. When GO sheets are restacked together, the hydrogen-bonded networks hold them tightly to generate a free-standing lamellar membrane. Within the laminates, the sp^2 clusters are connected across all the stacking layers to form a nano-capillary network, through which water molecules will experience an anomalous unimpeded trans-membrane permeation.[17,23] Due to the ionization of functional groups in water, GO membranes will be charged negatively, which will result in the attraction of cations and the repulsion of anions. In addition, the membranes prepared from single layered oxygen-functionalities decorated carbon sheets will be much lighter than the typical polymer-based ion exchange membranes. These unique properties make GO membranes suitable as ion-exchange membranes for the applications of waste water treatment and membrane separation.

In this paper, we demonstrate the effective recovery of acids from iron-based electrolytes using GO membranes which are composed of stacked microsize and nanosize GO flakes respectively, as illustrated in Figs. 1a,b. The mechanism for the different trans-membrane transportation of Fe^{3+} and H^+ was discussed.

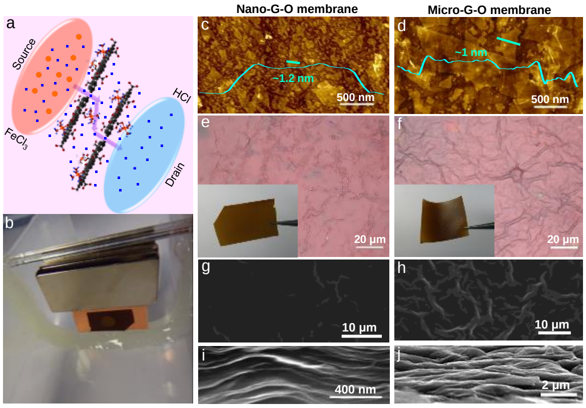

Figure 1. (a) Schematic drawing for the recovery of acids from iron-based electrolytes using GO laminates. (b) Photograph of the apparatus used for investigating the ion-transport through GO membranes. (c,d) AFM images of as-prepared nanosize and microsize GO sheets. The insets in (c) and (d) are height profiles of the corresponding flakes. (e,f) Optical images of nano- and micro-GO membranes drop-casted from nanosize and microsize flakes. The insets in (e,f) are the photographs of as-prepared nano- and micro-GO membranes. (g-j) SEM characterizations of the topographies and cross-sections of nano- and micro-GO membranes.

The microsize and nanosize GO sheets were synthesized by the modified Hummers' method from natural and worm-like graphitic flakes, respectively.[14,24] Figs. 1c, d exhibit the AFM characterizations of the as-synthesized micro- and nano-sized GO sheets. The insets reveal the single layer nature of these flakes. With these GO sheets, free-standing GO membranes were prepared by drop-casting 1.5 mg/mL GO aqueous solutions onto a smooth paper followed by drying and detaching off, as shown in the insets of Figs. 1e, f. The optical images and SEM characterizations for the topographies and cross-sections of the micro- and nano-GO membranes are shown in Figs. 1e-j, which reveal that the as-prepared micro- and nano-GO membranes possessed a wrinkled surface and lamellar structure. Notably, the amount of wrinkles decorated on micro-GO membranes was significantly larger than that on nano-GO membranes. The ion exchange capacity (IEC) was calculated for one of the GO membrane samples according to previous method[25] and we found that the IEC value was calculated to be ~4.4, which was significantly larger than the previous results[25], demonstrating the superior performances of GO membranes for the applications as ion exchange membranes. With these micro- and nano-GO membranes, the trans-membrane transport properties of iron-based electrolytes ($FeCl_3$) were investigated, as shown in Fig. 1b. Briefly, a plastic plate with an aperture (5 mm in diameter) in the center separated the source vessel from the drain vessel. A piece of GO membrane was sealed onto the aperture by double-faced copper tape with a matched hole in the middle so that GO membrane could connect the solutions in source and drain to facilitate the ion trans-membrane transport. During the experiments, 80 mL of $FeCl_3$ solution and deionized water were injected into the source and drain vessels respectively and the conductivity variations of the drains were measured at regular intervals (0.5 h) on a conductivity meter (INESA, DDS-307) to reflect the ion penetration behavior of the source solutions. The reason why we chose to study the penetration properties of $FeCl_3$ through GO membranes was that $FeCl_3$ electrolytes were adequate in steel industry and could be collected for reuse easily. More importantly, due to the intense hydrolysis of Fe^{3+} in solutions, abundant Fe^{3+} and H^+ ions would coexist, which facilitated the investigation of transportation of Fe^{3+} and H^+ ions through GO membranes synchronously.

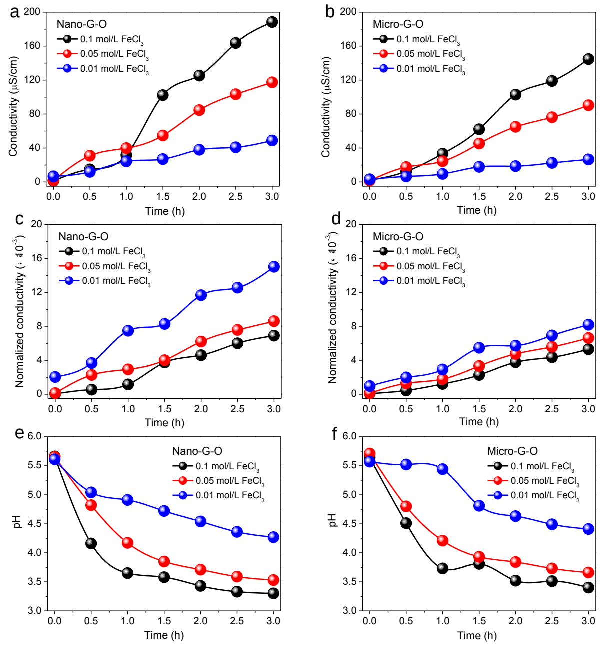

Figure 2. (a,b) Conductivity variations of the drains after permeating nano- and micro-GO membranes using $FeCl_3$ sources with different concentrations. (c,d) Corresponding normalized conductivity variations of (a,b). (e,f) pH variations of the drains after permeating nano- and micro-GO membranes using $FeCl_3$ sources with different concentrations.

Firstly, the ion penetrations through nano- and micro-GO membranes based on $FeCl_3$ sources with different concentrations were studied, as plotted in Figs. 2a and b. The result reveals that increasing the concentration of $FeCl_3$ sources from 0.01 to 0.1 mol/L led to the increase of conductivities in drains, indicating that the amount of ions migrating from source to drain increased with the source concentration. Notably, the conductivities of the drains for nano-GO membranes were larger than those for micro-GO membranes, which could be attributed to the increase of the amount of nanocapillaries formed within the membranes that facilitated the ion trans-membrane transportation when the lateral sizes of GO flakes were reduced from microsize to nanosize. Considering that the source conductivity would increase proportionately with the concentration in diluted solutions, normalized conductivities of the drains could be calculated by dividing by the corresponding source conductivities and plotted in Figs. 2c and d, which were utilized to compare the relative ion transport rates for $FeCl_3$ sources with different concentrations. Interestingly, it reveals in Figs. 2c and d that increasing the concentration of $FeCl_3$ sources resulted in the decrease of relative ion transport rates, which might be attributed to more Fe^{3+} cations aggregating within the nano-capillaries that blocked the migration of protons for higher source concentrations. Accompanied with the conductivity measurement, the pH values of the drain solutions were measured simultaneously, as plotted in Figs. 2e and f. They reveal that the pH values of the drains decreased with time and increasing the source concentration led to the decrease of drain pH values. In addition, the pH values of the drains for nano-GO membranes were smaller than those for micro-GO membranes, further demonstrating that the amount of nanocapillaries for the transport of protons in nano-GO membranes was greater than that for micro-GO membranes.

To further determine the accurate concentration of cations in drains after ion penetration through nano- and micro-GO membranes, the concentrations of protons were calculated by $c_{H+} = 10^{-pH}$, while the concentrations of Fe^{3+} in drains after penetration for 3 h were carried out by ICP analysis, as shown in Fig. 3. It reveals in Figs. 3a and b that during the ion trans-membrane transport process, the concentrations of protons in drains increased with time. As the concentrations of $FeCl_3$ sources were reduced, the concentrations of H^+ in drains decreased simultaneously. In contrast, the concentrations of Fe^{3+} in drains after penetration for 3 h were two orders of magnitude smaller than those of protons (Figs. 3c and d). Notably, when the concentrations of $FeCl_3$ sources were reduced to 0.01 mol/L, the concentrations of Fe^{3+} in drains for nano- and micro-GO membranes were both failed to detect by ICP analysis. These results indicated that the GO membranes could be used efficiently to recover acids from iron-based electrolytes with ultralow Fe leakage and the cycling penetrations could result in high purity acids. Generally, the production of acids from mixed salts is done with anion-exchange membranes by diffusion dialysis based on the fact that metallic cations are more or less impermeable to the anion-exchange membranes while protons can permeate the anion-exchange membranes easily. However, due to the enrichment of the fixed ions with positive charges within the anion-exchange membranes, the trans-membrane transport of protons is inevitably degraded by the electrostatic repulsions from the fixed ions with the same charges.

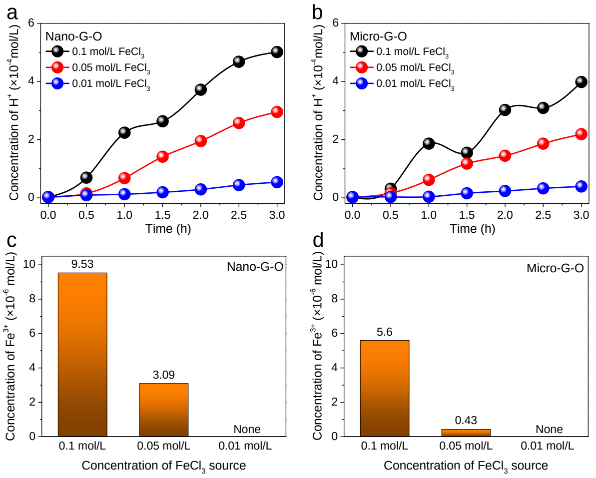

Figure 3. (a,b) Concentrations of H^+ in drains when penetrating through nano- and micro-GO membranes using $FeCl_3$ sources with different concentrations. (c,) The accurate concentrations of Fe^{3+} in drains after penetration for 3 h through nano- and micro-GO membranes with different $FeCl_3$ source concentrations.

Notably, in this study, GO membranes, as a new type of cation-exchange membrane, could be utilized for the recovery of high purity acids from mixed salts effectively, which distinguished this material from other traditional polymer-based ion-exchange membranes and might be used extensively in steel industry for reprocessing the spent pickling solutions. In addition, the concentrations of Fe^{3+} and H^+ were all greater for nano-GO membranes than for micro-GO membranes, indicating that the ion transport process could be tuned by the lateral dimension of GO sheets within the membranes.

Previously, we have demonstrated that GO membranes possessed selectivity towards different transition metallic cations, presumably due to the different coordination interactions between transition metal ions and *sp*^{3} C-O matrix of GO sheets.[18] In this case, due to the higher charges of Fe^{3+} cations, the coordination strength between Fe^{3+} and oxygen-containing functional groups attached on GO surfaces should be stronger, which led to the effective capture by C-O matrix of GO sheets when Fe^{3+} ions migrated into and through GO nanocapillaries and further led to the tiny amount of Fe^{3+} transporting through GO membranes and reaching the drains (Figs. 3c and d). On the other hand, according to a recent study by Joshi, et al[20], in aqueous environment, the GO membranes can act as molecular sieves to block all the solutes with hydrated radii lager than 4.5 angstroms. In the case of $FeCl_3$ sources, the hydrated radius of Fe^{3+} is 4.57 angstroms, which indicates that the strong confining effect of GO nanocapillaries to Fe^{3+} was also responsible for the effective blockage of Fe^{3+} cations. In contrast, the protons should follow a different mechanism to permeate GO membranes. During the ion trans-membrane transportation, the gradual humidification of the GO membranes should give rise to a larger interlayer spacing, which facilitated the formation of a hexagonal ice bilayer in between the GO flakes.[23] Along with the ice bilayer formation, the melting transition of ice at the edges of the sheets was proposed to be responsible for the anomalous unimpeded permeation of water through GO membranes.[23] In the case of proton transportation through GO membranes, the hydrophilic functional groups present in GO tended to attract H^+ ions, which should undergo fast propagation through the hydrogen-bonding networks along the water layers formed within the interlayer spacing.[26] These properties resulted in high proton migrations through GO membranes (Figs. 3a and 3b). The different mechanisms followed by the trans-membrane transport of Fe^{3+} and H^+ gave rise to the effective separation of H^+ from Fe^{3+}, which could be used to recover high purity acids from the spent pickling solutions in steel industry. In addition, when the lateral dimensions of the GO sheets used to form the membranes were reduced from micrometer to nanometer, the amount of nanocapillaries formed within the membranes should be increased significantly (as illustrated in Fig. 4), resulting in the enhancement of ion penetrations through GO membranes, as demonstrated in Figs. 2-3.

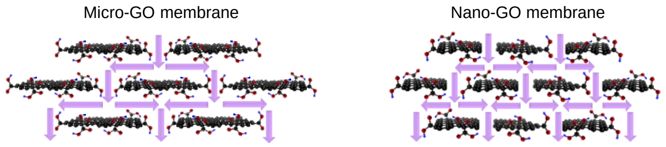

Figure 4. Schematic diagrams of the structure of nano-capillary networks in nano- and micro-GO membranes.

In conclusion, efficient recovery of acids from iron-based electrolytes using GO membranes was demonstrated. The trans-membrane transport of H^+ was two orders of magnitude greater than that of Fe^{3+}. Notably, when the concentration of $FeCl_3$ sources was reduced to some extent (*e.g.* 0.01 mol/L), the Fe^{3+} cations could be blocked by GO membranes entirely, suggesting that the cycling penetration of iron-based electrolytes could produce acids with high purity, which was superior to other traditional diffusion dialysis processes conducted by polymer-based anion-exchange membranes with serious Fe leakage. The mechanism for the effective separation of H^+ from Fe^{3+} was discussed, indicating that the molecular sieving effect of GO nanocapillaries and the coordination between Fe^{3+} and GO were responsible for the effective capture of Fe^{3+} while the rapid propagation of protons through the hydrogen-bonding networks along the water layers formed within the interlayer spacing was responsible for the fast migration of H^+. These unique properties of GO membranes make them promising as cation-exchange membranes for the applications of waste water reuse and membrane separation.

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Notes and references

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