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Improvement of Li/Mg monovalent ion selectivity of cation-exchange membranes by incorporation of cerium or zirconium phosphate particles

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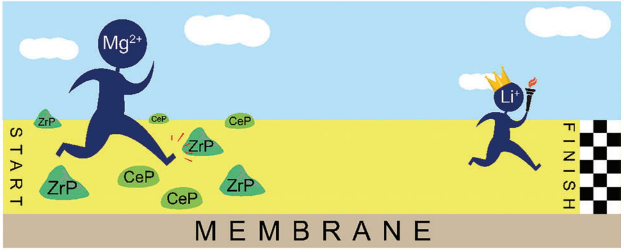
To improve the selectivity of cation-exchange membranes to the transfer of lithium with respect to magnesium during the electrodialysis desalination of lithium and magnesium sulfates solutions, the surface of a commercial cation-exchange membrane based on sulfated polystyrene was modified with cerium(III, IV) and zirconium phosphates. Upon incorporation of phosphate particles, the Li/Mg selectivity coefficients of the membranes increased up to 113%.



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The search for new ways to modify the selectivity of ion-exchange membranes (IEMs) for differently charged ions is of considerable interest.[1–4]

From the practical point of view, this modification increases the efficiency of membranes in the electricity generation by reverse electrodialysis due to exclusion of multivalent ions,[5] reduces fouling in the desalination of sea or river water by reducing the formation of insoluble salts,[6] and opens up prospects for selective zero-waste isolation of ions in the treatment of waste water.[7] A particularly relevant problem is to increase the selectivity of IEMs to lithium ions with respect to double-charged cations, such as magnesium or cobalt, for the use of electrodialysis in lithium separation from brines or products of treating lithium–ion batteries.[8–10] A method for the targeted modification of the selectivity of IEMs is to incorporate nanoparticles into a system of pores and channels. Previously,[11] we found that the incorporation of zirconium phosphate enhanced the Na/Ca selectivity; therefore, we expected a similar effect for the Li/Mg pair. The possibility of increasing the rate of chloride transfer relative to sulfate by modifying IEMs with cerium phosphate is also of interest.[12]

In this work, we were the first to perform the electrodialysis desalination of mixed Li/Mg solutions using hybrid cation-exchange membranes whose surfaces were modified with cerium and zirconium phosphates. A RALEX® cation-exchange heterogeneous membrane containing cross-linked sulfonated polystyrene as a conductive component was used as the base membrane.

The membranes were synthesized by the following methods: (1) one side of a membrane was saturated with Ce^{3+} ions by treatment with a cerium(III) nitrate solution, and the dopant was then precipitated by treatment of the same side with an ammonium dihydrogen phosphate solution (CEM–$Ce^{III}P$ sample) in a special cell for one-sided modification;[12] and (2) the membrane was saturated with a solution of cerium(VI) oxide in 85% orthophosphoric acid ($Ce^{IV}P$ solution), followed by precipitation of cerium phosphate with a dilute solution of ammonium dihydrogen phosphate (CEM–$Ce^{IV}P$ sample). The method is based on the synthesis of cerium phosphate from phosphoric acid based solutions of Ce^{IV}.[13] The corresponding samples of $Ce^{III}P$ and $Ce^{IV}P$ cerium phosphates were also obtained by similar methods outside the membrane matrix (Online Supplementary Materials, Table S1).

The synthesis of membranes surface-modified with zirconium phosphate was performed by saturating the membranes with ZrO^{2+} ions in zirconyl chloride solution followed by precipitation in an ammonium dihydrogen phosphate solution (CEM–ZrP sample)[11] in a cell for one-sided modification. A detailed description of all the experimental techniques for the synthesis and characterization of the membranes and a list of the equipment used are given in the Online Supplementary Materials.

According to powder X-ray diffraction (XRD) analysis, an individual sample of $Ce^{III}P$ corresponded to the rhabdophane phase $CePO_4{\cdot}H_2O$ (Figure S1), as was also confirmed by a cerium-to-phosphorus ratio of 1.04 obtained by wavelength-dispersive X-ray spectroscopy. According to thermogravimetry data for $Ce^{III}P$, 1.6 water molecules were lost by 300 °C due to the presence of 0.6 physically bound water molecules in the sample; no significant weight losses were then observed up to 800 °C [Figure 1(*a*)]. The presence of paramagnetic Ce^{3+} ions in the structure of $Ce^{III}P$ did not allow us to record the MAS ^{31}P NMR spectrum due to the coupling of the spins of ^{31}P nuclei with the paramagnetic centers, and the spectrum consisted of rotation artifacts (Figure S2).[14] According to pH titrimetry [Figure 1(*c*)], $Ce^{III}P$ had a minor ion-exchange capacity approximately estimated at 0.1–0.2 mmol g^{-1}, which also confirmed the formation of neutral cerium(III) phosphate.

Powder XRD analysis of the $Ce^{IV}P$ sample showed that it was weakly crystallized and had a very small particle size

(Figure S1). An intense line at 2θ of about 10° is characteristic of layered acid phosphates. According to elemental analysis, the phosphorus-to-cerium ratio was 1.5, while pH titration data showed a capacity close to 2 mmol g^{-1} [Figure 1(*c*)]. The ^{31}P NMR spectrum of Ce^{IV}P showed three signals due to phosphate groups coordinated with different numbers of cerium atoms [Figure 1(*b*)]. According to TGA data, the loss of 2.4 water molecules occurred by 300 °C [Figure 1(*a*)], above which several more steps of acid phosphate decomposition were observed due to dehydration, polycondensation of phosphate anions, and reduction of Ce^{IV} to Ce^{III}.[13] In combination, this is indicative of the formation of acid cerium(IV) phosphate with the formula $H_xCe^{IV}(PO_4)_{1.5} \cdot 2.4H_2O$.

Individual zirconium phosphate was not synthesized in this work, but it was characterized previously[11] as an amorphous acid zirconium phosphate with a P/Zr ratio of 2.1.

The incorporation of cerium and zirconium phosphates and the surface character of modification were confirmed using scanning electron microscopy with element distribution mapping and attenuation total reflectance (ATR) IR spectroscopy. Element mapping showed that cerium/zirconium phosphates were heterogeneously distributed through depth and concentrated near the modified surfaces [Figure 2(*a*)]. Moreover, phosphorus and cerium/zirconium were distributed identically to indicate the formation of the required phosphates. Note that the distribution maps contained dark areas due to the elements of the reinforcing polypropylene mesh of the base membrane. According the of X-ray microanalysis data, the phosphorus-to-cerium atomic ratios in CEM–Ce^{III}P and CEM–Ce^{IV}P were 0.98 and 1.6, respectively, which are consistent with the elemental compositions of the individual powders.

An analysis of the ATR IR spectra of unmodified and modified membranes allowed us to judge unequivocally the course of surface modification because absorption bands at 600–640 and 1000 cm^{-1} corresponding to the bending and stretching vibrations of phosphate groups[15] were recorded on one side of a membrane. The peak intensity of phosphate groups (and hence the concentration of phosphates in the surface layers) increased in the order CEM–Ce^{IV}P < CEM–Ce^{III}P < CEM–ZrP.

Incorporation of neutral phosphate Ce^{III}P resulted in a significant decrease in the ion-exchange capacity (IEC), water uptake, and conductivity of the CEM–Ce^{III}P membrane (Table 1). The ion-exchange capacity decreased by 27% due to the formation of $R–SO_3^{-}\cdots Ce^{III}P$ salt bridges between phosphate particle surface and the functional groups of the membrane pore. A similar phenomenon was observed upon the incorporation of cerium and zirconium oxides[11,16] or zirconium phosphate with small concentrations of phosphorus groups[11] into the cation-exchange membranes. The conductivity and water uptake of Ce^{III}P also decreased due to the blockage of a part of ionogenic centers. At the same time, Ce^{IV}P and ZrP acid phosphates that have cation-exchange groups did almost not decrease these parameters or even increased them.

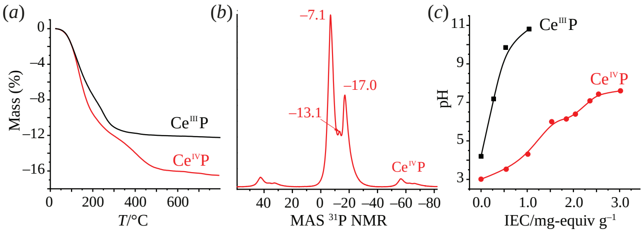

Figure 1 (*a*) Mass *vs*. temperature plot, (*b*) MAS ^{31}P NMR spectrum, and (*c*) dependence of the ion-exchange capacity of individual Ce^{III}P and Ce^{IV}P powders on pH.

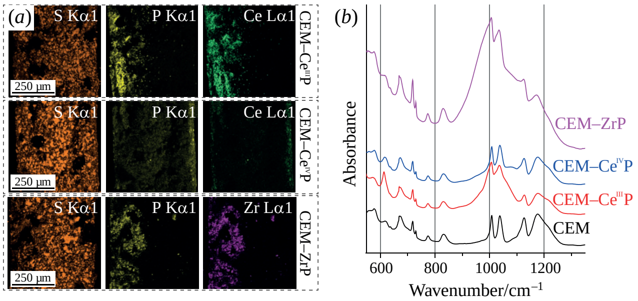

Figure 2 (*a*) Distribution of sulfur, phosphorus, and cerium/zirconium in the membranes; (*b*) ATR IR spectra of original and hybrid membranes (modified sides).

A comparison of the two methods of cerium phosphate incorporation showed that the dopant amounts were the same in the cases of one-sided modification of CEM–Ce^{III}P and two-sided modification of CEM–Ce^{IV}P. This was due to the fact that Ce^{3+} from a cerium(III) nitrate solution penetrated into the membrane much better than Ce^{IV} from a solution in 85% orthophosphoric acid because a significant fraction of Ce^{IV} in the acid occurred in the anionic form of phosphate complexes. In addition, the membrane dehydration in concentrated orthophosphoric acid was accompanied by a decrease in pore size and, hence, ion diffusion coefficients, which reduced the efficiency of this kind of treatment.

In a model electrodialysis desalination, the original membrane had a high selectivity for magnesium ion transfer, especially, in dilute solutions where the Li/Mg selectivity coefficient was lower than 0.1. The incorporation of phosphates increased the selectivity to lithium in both concentrated and dilute solutions, where this effect was markedly higher [Table 1, Figure 1(*b*)]. However, the effect of cerium phosphates on selectivity was small, whereas zirconium phosphate increased it by a factor of more than 2 in dilute solutions.

Previously we found that the higher concentration of acid phosphate groups in the incorporated zirconium phosphate, the more efficient the inhibition of the transfer of double-charged calcium ions with respect to single-charged sodium ions.[11] By a direct analogy to the test system, the small effect of Ce^{III}P on selectivity in the Li/Mg pair can be attributed to its neutral nature and the lack of participation of phosphate groups in the ion transport process.

Thus, we found that the incorporation of cerium or zirconium phosphates into a matrix of cation-exchange membranes increased the transport selectivity of lithium ions relative to that of magnesium. At a lower concentration in the surface layer, cerium(IV) acid phosphate had an effect on the selectivity similar in intensity to that of neutral cerium(III) phosphate. However, a significantly higher selectivity was observed in the hybrid membrane with acid zirconium phosphate where the phosphate content of the surface layer was the highest.

Table 1 Dopant concentration (W_d), water uptake (*WU*), ion-exchange capacity (IEC), ionic conductivity [σ(Li)], and selectivity coefficients [*P*(Li/Mg)] of the membranes.

Sample	W_d (%)	*WU* (%)	IEC/ mg-equiv g^{-1}	σ(Li)/ mSm cm^{-1}	*P*(Li/Mg)^a in 0.04 M	*P*(Li/Mg)^a in 1.0 M
RALEX® CEM	–	59.3	2.36	4.9	0.075	0.42
CEM–Ce^{III}P	1.8	57.3	1.73	3.9	0.084	0.45
CEM–Ce^{IV}P	1.7	59.2	2.22	4.6	0.081	0.46
CEM–ZrP	3.0	61.2	2.26	4.5	0.16	0.77

^{a} The selectivity coefficient *P*(Li/Mg) was calculated as a ratio between the fluxes of lithium and magnesium divided by the average concentration ratio between these ions in a desalting compartment. A mixture of Li_2SO_4 and $MgSO_4$ with the starting ratio Li : Mg = 1 : 1 was used. The detailed calculation is described in the Online Supplementary Materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.04.022.

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