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

Andrey D. Manin, Daniel V. Golubenko, Polina A. Yurova and Andrey B. Yaroslavtsev

Experimental

Materials and equipment

A commercial cation-exchange membrane RALEX® CM (MEGA, Czech Republic) was used. Membranes of this type are based on a composite of sulfostyrene-divinylbenzene cation-exchange resin particles dispersed in a polyethylene matrix. The thickness of the swollen film was 711 μm and the water uptake was ca. 37.2 wt%. The following reagents were used in the study: sodium chloride (Khimmed, "chemically pure"), cerium(III) nitrate hexahydrate (99.999% trace metals basis, Sigma–Aldrich), zirconyl chloride octahydrate (98%, Sigma–Aldrich), ammonium phosphate monobasic (ACS reagent ≥98%, Sigma–Aldrich), urotropine (Khimmed, "chemically pure"), phosphoric acid 85% (Khimmed, "chemically pure"), hydrochloric acid (Khimmed, "chemically pure"), sodium nitrate (Khimmed, "chemically pure"), sodium hydroxide (Khimmed, "chemically pure"), and phenolphthalein indicator.

Techniques for the synthesis of cerium phosphate and modified membranes

Synthesis of cerium phosphate

Since it is difficult to study cerium phosphates within hybrid membranes, the corresponding samples were obtained separately under conditions similar to those of the synthesis of phosphates in membranes. Two different cerium phosphates were studied in this work:

Table S1. Composition of precursor solutions

Name of compound	Cerium reagent	Phosphorus reagent
$Ce^{(III)}P$	0.15 M solution of $Ce(NO_3)_3$	0.5 M solution of $NH_4H_2PO_4$
$Ce^{(IV)}P$	0.15 M solution of CeO_2 in 85% H_3PO_4	1.0 M solution of $NH_4H_2PO_4$

$Ce^{(III)}P$ was obtained by dropwise addition of a $Ce(NO_3)_3$ solution to a $NH_4H_2PO_4$ solution with stirring; the reagents were taken in a molar ratio of Ce:P = 3:50. After four hours of stirring, the precipitate that formed was allowed to settle for 24 h. Subsequently, it was washed several times with 0.1 M HCl solution with stirring to replace the ammonium cations in the phosphate structure by protons. After that, the resulting suspension was freed from the mother liquor by repeated washing with distilled water to a neutral pH by centrifugation/re-dispersion on Centrifuge

5804 (Eppendorf, Germany). The resulting precipitate was dried in an oven for 12 h at 40°C. As a result, a white powder was obtained.

$Ce^{(IV)}P$ was obtained by a technique previously developed by Ivanov et al.[S1] Cerium(IV) oxide obtained by homogeneous precipitation from a $Ce(NO_3)_3$ + hexamethylenetetramine solution[S2] was dissolved with stirring in concentrated (85%) orthophosphoric acid preheated to 120°C. The resulting transparent yellowish solution ($Ce^{(IV)}P$-solution) containing 0.15 M cerium was added dropwise with stirring to 1 M solution of ammonium dihydrophosphate; the reagents were taken in a molar ratio of Ce:P = 1:100. Once the entire amount of $Ce^{(IV)}P$-solution was added, stirring was stopped. After 8 h, a fraction of the mother liquor was decanted, distilled water was added, the mixture was stirred for another 1 h, allowed to settle, and a fraction of the mother liquor was decanted again. This operation was repeated until a neutral pH was reached. The resulting suspension was freed from the mother liquor by repeated washing with distilled water to a neutral pH by centrifugation/re-dispersion on Centrifuge 5804 (Eppendorf, Germany). The resulting precipitate was dried in an oven for 12 h at 40°C. As a result, a grayish-green powder of $Ce^{(IV)}P$ was obtained.

Synthesis of hybrid membranes

Three hybrid membranes were obtained in this work.

The CEM-$Ce^{(III)}P$ membrane was obtained by analogy with the technique that we suggested previously.[S3] Namely, as received membrane sample was kept for three days in saturated sodium chloride solution. Prior to the modification, the concentration of sodium chloride solution was reduced to 0.15-0.2 M by successive dilution in a few hours. The membrane ready for modification was mounted in a special cell. A 0.2 M sodium chloride solution was kept on one side of the membrane, while on the other side it was successively treated with 0.15 M $Ce(NO_3)_3$ and 0.5 M $NH_4H_2PO_4$ solutions, for 10 min in each. After the treatment, the membrane was removed from the cell and kept for 12 h in 0.5 M $NH_4H_2PO_4$ solution.

The CEM-$Ce^{(IV)}P$ membrane was obtained by treatment of the as received membrane in CeP-solution for 60 min followed by aging for 12 h in 1 M NH_4H_2PO solution.

The CEM-ZrP membrane was obtained in the same way as the CEM-$Ce^{(III)}P$ membrane, but the surface being modified was successively treated with 1.0 M $ZrOCl_2$ solution and 0.5 M $NH_4H_2PO_4$ solution, for 30 min in each [S4]. After the treatment, the membrane was removed from the cell and kept for 40 h in 0.5 M $NH_4H_2PO_4$ solution.

All the hybrid membranes thus obtained were conditioned by repeated washing in 0.5 M NaCl solution.

Instrumental methods

The IR spectra of the samples being studied were recorded with a Nicolet iS5 spectrometer (Thermo Scientific, USA) with a Quest Specac accessory in ATR (attenuation total reflectance) mode. The morphology of the membranes thus obtained was studied by scanning electron microscopy using a TESCAN AMBER GMH scanning electron microscope (TESCAN, Czech Republic) equipped with an energy dispersive microanalyzer unit. Membrane cross-sections for studying the element thickness distribution was prepared by cutting samples cooled to liquid nitrogen temperature with scissors. Powder X-ray diffraction analysis was performed using a D/MAX 2200 diffractometer (Cu-Kα) (Rigaku, Japan). Thermogravimetric analysis was performed in the temperature range of 25-800°C on a TG 209 F1 instrument (Netzsch, Germany). MAS ^{31}P NMR spectra were measured with an AV400 instrument (Bruker Co., USA) at a sample holder rotation frequency of 9 kHz. The elemental composition was determined using a Spectroscan Max-GVM wavelength-dispersive X-ray spectroscope (NPO SPECTRON, Russia).

Characterization of cerium phosphate and hybrid membranes

Ion exchange capacity of cerium phosphate

The ion-exchange capacity of the phosphates obtained was determined by potentiometric titration, i.e. a study of the dependence of the pH of a solution in which cerium phosphate is dispersed *vs*. the amount of sodium hydroxide added. Each point of the cerium phosphate titration curve was obtained as follows. A sample of cerium phosphate (ca. 25 mg) was placed in a plastic container, a required amount of 0.1 M NaOH solution was added, the volume of the solution was adjusted to 15 ml by adding 0.1 M NaCl solution, and the solution was stirred for 24 hours with an orbital shaker. After that time, the solution pH was measured with an “Expert-pH” pH-meter (Econix-Expert, Russia). The sorption ion-exchange capacity in each point was calculated using the formula:

$$Q(CeP) = \frac{C(NaOH)\cdot V(NaOH)\cdot 1000}{m} \quad (1)$$

where $Q(CeP)$ is the ion-exchange capacity (mmol/g), $C(NaOH)$ is the concentration of sodium hydroxide solution, $V(NaOH)$ is the alkali volume added, and m is the mass of the phosphate.

Ion exchange capacity of membranes

Before studying the ion exchange capacity of the membranes, they were converted to the proton form by treatment with 0.1 M hydrochloric acid solution with triple acid replacement, after which the excess acid was washed off with deionized water. To remove the excess moisture, the membrane surface was blotted on both sides with filter paper, after which the membrane samples were placed in 1.0 M $NaNO_3$ solution for a few hours while stirring with a shaker. The concentration of protons released during the ion exchange reaction was then determined

titrimetrically in the presence of phenolphthalein using 0.01 M NaOH solution as the titrant. The volume of the sodium nitrate solution was chosen in such a way that the concentration of nitrate ions was about 50 times higher than the final concentration of protons (about 0.01 M) to ensure almost complete displacement. The ion-exchange capacity was calculated using the formula:

$$Q = \frac{V(NaNO_3) \cdot C}{m_{dry}} \quad (2)$$

where *Q* is the ion-exchange capacity of the membrane (mmol/g), *V(NaNO₃)* is the volume of sodium nitrate solution added, *C* is the concentration of protons, and m_{dry} is the mass of the dry membrane.

Water uptake

The water uptake was determined for membranes in the Na-form. First, membrane samples were equilibrated with distilled water. The mass of a hydrated membrane was measured on an ALC-2104d analytical balance (Acculab Sartorius group, USA). To remove excess moisture, the membrane surface was blotted with filter paper on both sides. The procedure was repeated four times to obtain an averaged value. Next, the membranes were dehydrated in an ES-4610 Drying Oven (ECROSKHIM LTD, Russian Federation) for 1.5 hours at 80°C, after which the mass of dry membranes was measured. The water uptake was calculated using the formula:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\% \quad (3)$$

where WU is the water uptake, m_{wet} is the mass of the hydrated membrane, and m_{dry} is the membrane mass after drying.

Dopant content in membranes

To determine the content of the inorganic dopant, the membranes were converted to protonic form by incubating the samples in 0.1 M HCl solution, then equilibrated with deionized water. The samples were cut into small pieces and annealed for 8 h in a muffle furnace at 800°C. After the heat treatment was completed, the mass of the ash was measured. The dopant percentage in the membrane was calculated by the formula:

$$\omega_d = \frac{m_{ash}}{m_{mem}} \cdot 100\% \quad (4)$$

where ω_d is the percentage of cerium phosphate, m_{ash} is the mass of the inorganic ash, and m_{mem} is the mass of the dry membrane before annealing.

Ionic conductivity of membranes in the Li^+ form

To determine the conductivity of the membranes, they were first converted to the corresponding ionic form by keeping in 0.1 M Li_2SO_4 solution followed by equilibration with deionized water. A membrane sample was then placed between two steel electrodes and mounted in a special cell that was placed in a beaker with deionized water at 22.4-22.8°C and thermostatted for 5 minutes, after which the ionic conductivity was measured by impedance spectroscopy. The measurements

were carried out using an Elins Z-1500J alternate current bridge (Elins, Russia) in the frequency range of 500 kHz – 10 Hz. The resistance was determined from the intercept with the active impedance axis in Nyquist coordinates.

Li/Mg selectivity of membranes

The Li/Mg selectivity of membranes was determined in the model ED desalination of an equinormal solution of a mixture of lithium and magnesium sulfates in a four-compartment laboratory cell by a procedure similar to that published previously.[S5] At the beginning of desalination, the diluate compartment was filled with an equinormal solution of lithium and magnesium sulfates with a total cation concentration of 0.04 M or 1.0 M. The concentrating compartment was filled with a K_2SO_4 solution with 0.04 M or 1.0 M total concentration of K^+ ions. A membrane was placed in the cell so that the modified side was in contact with the desalted solution; RALEX® AM membranes separated the concentrate and diluate from the electrode sections. The active area of the membrane in question was 4.90 cm^2. The volume of the solution in each of the concentrating and desalination compartments was 40.0 ml. Stirring was performed with a self-made two-position magnetic stirrer. 0.2 M K_2SO_4 was used as the electrode solution that was pumped at a rate of 300 ml/min through the electrode compartments. Before desalination, the membranes studied were equilibrated in an appropriate solution of a mixture of lithium and magnesium sulfates, then desalination was performed in galvanostatic mode for 60 min, the solutions in both chambers were renewed and a similar desalination was performed for the next 200 minutes. The first desalination step is required to equilibrate the membrane under electrodialysis desalination conditions. The currents for the 0.04M and 1.0M solutions were 0.82 and 20.4 mA/cm^2, respectively. The current was set using a P-40X potentiostat-galvanostat (Elins, Russia). At the end of the experiment, the concentration of lithium and magnesium ions in the concentrating chamber was determined by ion chromatography (Stayer ion chromatography system, Akvilon company). The values of lithium and magnesium concentrations obtained upon desalination of the membranes are given in Table S2.

Table S2. Values of lithium and magnesium concentrations in the concentrating chamber upon desalination with the membranes studied

Sample	0.04M		1.0M	
	C(Li) in conc. compartment, M	C(Mg) in conc. compartment, M	C(Li) in conc. compartment, M	C(Mg) in conc. compartment, M
RALEX® CM	0.00153	0.0139	0.0786	0.167
CEM-$Ce^{(III)}$P	0.00148	0.0126	0.0672	0.142
CEM-$Ce^{(IV)}$P	0.00123	0.0112	0.0801	0.161
CEM-ZrP	0.00128	0.0080	0.0921	0.116

The selectivity coefficient P_{Mg}^{Li} is expressed as follows:[S6]

$$P_{Mg}^{Li} = \frac{J_{Li^+}}{J_{Mg^{2+}}} \cdot \frac{C_{Mg^{2+}}^{av}}{C_{Li^+}^{av}} \quad (5)$$

where J_{Li^+} is the flux of Li^+ ions, $J_{Mg^{2+}}$ is the flux of Mg^{2+} ions, $C_{Li^+}^{av}$ is the mean concentration of Li^+ ions in the desalination compartment, and $C_{Mg^{2+}}^{av}$ is the mean concentration of Mg^{2+} ions in the desalination compartment.

Based on the experimental ion concentrations in the concentrating and desalination compartments at the end of the experiment and expression (5), the Li/Mg-selectivity factor P_{Mg}^{Li} was calculated using the formula:

$$P_{Mg}^{Li} = \frac{C_{Li^+}^{conc}}{C_{Mg^{2+}}^{conc}} \cdot \frac{C_{Mg^{2+}}^{0} + (C_{Mg^{2+}}^{0} - C_{Mg^{2+}}^{conc})}{C_{Li^+}^{0} + (C_{Li^+}^{0} - C_{Li^+}^{conc})} \quad (6)$$

where $C_{Li^+}^{conc}$ is the concentration of Li^+ ions in the concentrating compartment after desalination, $C_{Mg^{2+}}^{conc}$ is the concentration of Mg^{2+} ions in the concentrating compartment after desalination, $C_{Li^+}^{0}$ is the starting concentration of Li^+ ions in the diluate compartment before desalination, and $C_{Mg^{2+}}^{0}$ is the starting concentration of Mg^{2+} ions in the diluate compartment before desalination.

Experimental data

Structure and properties of cerium phosphate

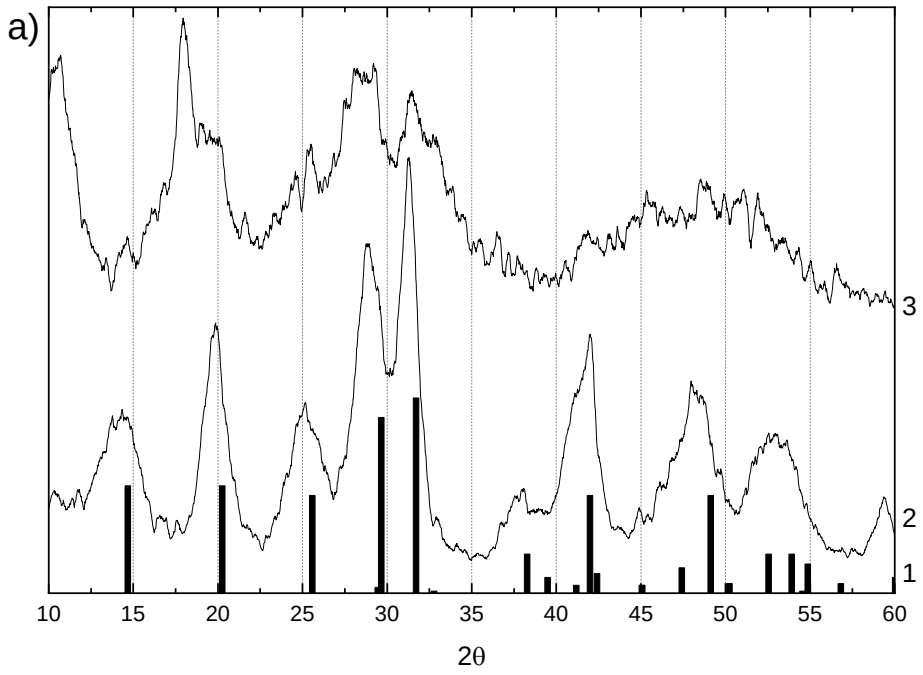

Figure S1. Reference diagram of $CePO_4 \cdot H_2O$ (*1*, PDF-2 Data Base) and XRD pattern of $Ce^{(III)}P$ *(2)*, $Ce^{(IV)}P$ *(3).*

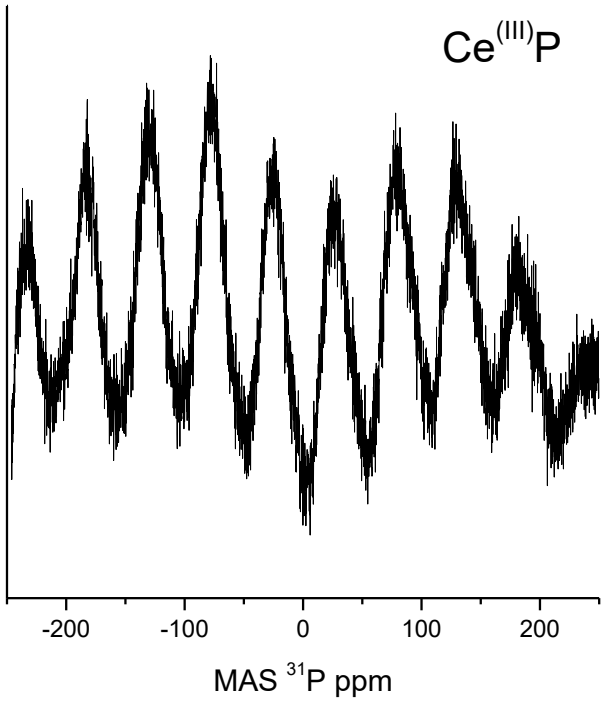

Figure S2. MAS ^{31}P NMR of $Ce^{(III)}P$

Table S3. Content of cerium and phosphorus in samples of cerium phosphate (mass%) determined by X-ray fluorescence spectroscopy

Sample	Ce mass%	P mass%	P:Ce atomic
$Ce^{(III)}P$	81.31	18.69	1.04
$Ce^{(IV)}P$	75.01	24.99	1.507

Table S4. P/Me atomic ratios in samples of hybrid membranes determined by X-ray spectral microanalysis

Sample	P:Me atomic
CEM-$Ce^{(III)}P$	0.98
CEM-$Ce^{(IV)}P$	1.6
CEM-ZrP	1.7

References

S1 T. O. Shekunova, A. E. Baranchikov, O. S. Ivanova, L. S. Skogareva, N. P. Simonenko, Yu. A. Karavanova, V. A. Lebedev, L. P. Borilo and V. K. Ivanov, *J. Non-Cryst. Solids*, 2016, **447**, 183.

S2 O. S. Polezhaeva, N. V. Yaroshinskaya and V. K. Ivanov, *Inorg. Mater.*, 2008, **44**, 51.

S3 D. V. Golubenko, A. D. Manin, Y. Wang, T. Xu and A. B. Yaroslavtsev, *Desalination*, 2022, **531**, 115719.

S4 D. V. Golubenko, Yu. A. Karavanova, S. S. Melnikov, A. R. Achoh, G. Pourcelly and A. B. Yaroslavtsev, *J. Membr. Sci.*, 2018, **563**, 777.

S5 D. Ding, A. Yaroshchuk and M. L. Bruening, *J. Membr. Sci.*, 2022, **647**, 120294.

S6 Y. Tanaka, *Ion Exchange Membranes: Fundamentals and Application*, 2nd edn., Elsevier, Amsterdam, 2015.