Inorganic Anion Exchange Membrane Prepared from Hydrotalcite Like Compounds

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Summary

Inorganic anion exchange membranes were prepared from the powdered hydrotalcite like materials as anion exchangers and polyvinylidene fluoride as a binder for the membrane fabrication. Following hydrotalcite like materials (combination of di- and tri-valent metal ions) were prepared, Mg(II)-Al(III), Ni(II)-Al(III), and Co(II)-Al(III) systems. Each powdered material was dispersed in dimethylformamide solution of polyvinylidene fluoride and spreaded on a glass dish to form a membrane. The electric resistance measured was ranging 200–700 $\Omega\cdot\text{cm}^{-2}$ and 80–150 $\Omega\cdot\text{cm}^{-2}$ at 25°C and 80°C, respectively. The plots of membrane potential vs. log of NaCl activity were linear between 10$^{-3}$ - 1 mol·dm$^{-3}$. The transport numbers for Cl$^-$ ions were around 0.94 at 80°C which approached 0.99 for the commercially available organic anion exchange membrane. The thermal stability was superior to that of organic anion exchange membrane.

1 Introduction

Inorganic ion exchange materials have their own historical significance. The ion exchange phenomenon was first observed in inorganic soils$^1$. The inorganic ion exchange materials, however, were not used for the practical purposes for they generally have slow exchange rate and small exchange capacity in addition to the difficulty in molding desired shapes. The development of the ion exchange materials was then transferred to the organic ion exchange materials. Recently, the potential importance of the inorganic ion exchange materials began to increase simultaneously with the development of new types of ceramic materials such as those in electronic devices. Since the ionorganic ion exchange materials are superior to the organic ones in the selectivity between similar metal ions, thermal resistivity, mechanical strength, and resistance for irradiation, they may be endure for industrial use if specific situations are encountered. Zeolites, zirconium phosphates$^8$, three types of antimonious acids$^9$, various potassium titanates$^10$, and spinel type manganese oxides$^9$ are typical examples.

Considering the peculiarities of inorganic materials, the preparation of inorganic ion exchange membranes has been intended. Few inorganic ion exchange membranes which were prepared without using any organic materials were reported. Simple pressure molding procedures$^8$, for example, were examined though the dense membrane without any
leakage was unsuccessful. A sol-gel method was adopted to prepare antimonic acid membrane using porous alumina support\(^7\). However, the densness of the membrane was still insufficient.

A variety of inorganic cation exchange materials are known so far such as zeolites, clay minerals, transition metal(IV) phosphates, three kinds of antimonic acid, potassium titanates, etc. Amphoteric inorganic ion exchangers are also known in various compounds. However, few inorganic compounds which exhibit pure anion exchange properties are known. Hydrotalcite like compounds which are complex hydrous oxides composed of divalent metal cations and trivalent metal cations are very few examples of such inorganic anion exchange materials\(^8\). Mg(II) -Al(III) system is one of the most common hydrotalcite like compounds and is a naturally available compound. Other combination of metal ions between M(II) and M(III) are also known although few informations on the anion exchange property have been reported\(^9\) -\(^11\). For example, no report has been published which suggested the presence of pure OH\(^-\) form hydrotalcite like compounds or much less which proved the ion-exchange ideality between OH\(^-\) and other anions.

Among ion exchange membranes, it is known that the thermal resistivity of anion exchange membranes is especially poor. This paper deals with the preparation of inorganic anion exchange membranes using hydrotalcite like compounds as anion exchanagers and polyvinylidene fluoride as a binder which is more stable at high temperature than the ordinary anion exchange materials. The physical characterizations of the products and the measurements of the electrochemical properties such as transport number are carried out.

### 2 Experimental

**Preparation of Cl\(^-\) form hydrotalcite like compounds:** Three types of hydrotalcite compounds (HT) in CO\(_3^{2-}\) form were prepared in advance. 0.35 M (M=mol\(\cdot\)dm\(^{-3}\)) M(II)Cl\(_2\) and 0.15 M M(III)Cl\(_3\) mixed solution was mixed with 0.2 M NaOH solution. All reagents used were of reagent grade (Wako Pure Chemical Ind. Ltd., Japan). The mixtures were thoroughly stirred during the reaction and then aged for 24 h. They were washed with the deionized water and air dried. The prepared samples contained much CO\(_3^{2-}\) and were termed CO\(_3^{2-}\) form hydroalcites although they contained other exchangeable anions such as Cl\(^-\). The CO\(_3^{2-}\) form hydrotalcites (Ni(II) -Al(III) and Co(II) -Al(III)) were treated by diluted HCl solution carefully to produce Cl\(^-\) form ones. After the carefull HCl treatment, they were dried at 60\(^\circ\)C for 2 days and ground to pass a 53 \(\mu\)m sieves to serve membrane formation. Commercially available CO\(_3^{2-}\) form Mg(II) -Al(III) hydrotalcite (KW-500 (Mg\(_{4.5}\)Al\(_2\) (OH)\(_{13}\)CO\(_3\) • 3.5H\(_2\)O; Kyowa Chemical Ind. Ltd., Japan) was used\(^12\). The Cl\(^-\) form Ma-Al hydrotalcite was prepared in different procedure. It was calcinated at 500 \(^\circ\)C for 1 h in advance. After calcination, the sample was soaked in the 1 M NaCl at room temperature to transform into Cl\(^-\) one.

**Chemical analysis and characterization:** The chemical analysis of metal ions for hydrotalcite like compounds were carried out using ICP (inductively coupled plasma) photoemission spectroscopy. The prepared samples were characterized using X-ray diffraction analysis, FT-IR, and thermal analyses (thermogravimetry (TG) and differential thermal analysis (DTA)).

**Preparation of membranes:** Polyvinylidene fluoride (PVF: Aldrich Chemical Co. Inc., U. S. A.) was selected as the binder because reliable informations about the thermal and chemical stability of this materials are available. Dimethylformamide (DMF: Kanto Chemical Co., Inc. Japan) was selected as a solvent to dissolve PVF in this study because DMF is a superior solvent for this compound. The optimum mixing processes and aging time were determined empirically in this study from many series of sample preparation under different conditions. The optimum weight ratio of [PVF] / [HT] was found to be 1.25. Hydrotalcite membranes using PVF were prepared as follows. Polyvinylidene fluoride was dissolved homogeneously in DMF solvent with stirring for 20 min. HT powders ground to 53 \(\mu\)m sieves were then mixed with PVF - DMF solution and stirred mechani-
cally for 20 min. The resulting suspension of HT was spreaded on a flat glass dish and dried at 80°C for 1 day to form the dense and tight membrane (HT/PVF membrane). The average thickness of the membranes prepared was about 0.2 mm. The dried membrane was cut out in 1.5 cm square and served for the various measurements. The mechanical strength of this membrane was sufficient for the application to various electrolytic processes.

**Electric resistance:** The electric resistance of HT/PVF membranes were measured by AC impedance method operated at 1 kHz. The resistance of the membranes was determined by subtracting the resistance of the electrolyte solution from that mounted by HT membranes. In AC method, the measurements were carried out using a cell consisted of two chambers (effective area was 0.78 cm²) as shown in Fig.1 and electrodes used were ruthenium coated titanium electrodes (Permelec Electrode, Ltd. Japan). The measurement was made on 0.1 M NaCl solution where membranes were equilibrated with the respective solutions for 1 day or more before measurements. The measurement of the electric resistance was carried out at 25, 60, and 80°C, respectively.

**Transport number:** The transport number of Cl⁻ anion was determined by measuring the membrane potential of the NaCl concentration cell. The schematic view of the concentration cell is shown in Fig.2. The reference electrodes in both compartments were KCl saturated silver/silver chloride electrodes. The reference solution was 0.1 M NaCl solution and the concentration of the test solution was varied from $10^{-3}$ M - 1 M. Each solutions were flowed with a constant flow rate for 6 min and the potential difference across the membrane was recorded 6 min after the interruption of the solution flow. The transport number were estimated from the slope of the potential difference vs. log of NaCl activity according to the standard procedure using the equations of the membrane potential.

## 3 Results and Discussion

### 3.1 Chemical analysis and characterization of hydrotalcites

**Chemical analysis:** The metal ion ratios [M(II)/
M(III) in mole ratio] of the hydrotalcite like compounds prepared were analyzed chemically. The results of M(II)/M(III) ratio were 2.8 and 2.9 for CO₃²⁻ form Ni-Al and Co-Al hydrotalcites, respectively. On the other hand, they were 2.33 and 2.50 for Cl⁻ form hydrotalcites. These values indicated that these compounds had typical chemical formula as hydrotalcite like compounds.

X-ray diffraction analysis: Commercially available Mg-Al hydrotalcite which typically has a following chemical formula was used.

\[ \text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3\cdot3.5\text{H}_2\text{O} \]

Generally speaking, the compound contains about 2 water molecules per unit valence of exchangeable anions. In the above case, average 1.75 water molecules exists per 1/2 (CO₃)⁻². Most of the hydrotalcite like compounds reveal similar X-ray diffraction patterns irrespective of parent di- and tri-valent metal ions. The crystal system can be approximated to be a hexagonal lattice in which layers lie perpendicular to the c axis. Strictly speaking the crystal systems may be of monoclinic where c axis slightly tilts against a-b plane⁹,¹³.

Figure 3 shows the result for the HCl or NaCl treated samples. They coincided well to that reported previously. Co-Al HT showed a very sharp peak around 12° (Cu-Kα) though any detectable peaks were not observed above 30° in this HT. This pattern might suggest the partial decomposition during HCl treatment. Totally speaking, crystallinity of our sample was not so bad.

IR spectra and TG-DTA data: The IR spectra were measured to confirm the transformation from CO₃⁻ form to Cl⁻ one. Figures 4 show the result. In Mg-Al and Ni-Al HTs the peak attributable to ν₃ mode for CO₃⁻ or HCO₃⁻ (1350 - 1380 cm⁻¹) decreased appreciably though detectable CO₃⁻ still remained. The ν₃ mode completely disappeared in Co-Al HT and suggested that the transformation into Cl⁻ form occurred completely in this system.

Figures 5 (a) - 5 (c) show the thermal analysis data (TG and DTA). A very large endothermic peak around

![Figure 3](image3.png)

**Fig.3** X-ray diffraction patterns of hydrotalcite like compounds in Cl⁻ form. a) Mg-Al, b) Ni-Al, c) Co-Al.

![Figure 4](image4.png)

**Fig.4** IR spectra of hydrotalcite like compounds before and after Cl⁻ treatment. a) Mg-Al, b) Ni-Al, c) Co-Al.
Fig. 5 TG and DTA curves of hydrotalcite like compounds in Cl- form. a) Mg-Al, b) Ni-Al, c) Co-Al.

320°C suggested the desorption of interlayer water molecules in Mg-Al and Ni-Al HTs. On the other hand, such a peak was ambiguous in Co-Al HT. The results of DTA as well as X-ray diffraction analysis suggested the partial decomposition of hydrotalcite lattice in Co-Al HT. Since the presence of hydrotalcite lattice was obvious in X-ray analysis, electrochemical measurements were also carried out in Co-Al HT.

3.2 Electric resistance

The electric resistance was measured by AC impedance method in 0.1 M NaCl solution at three temperatures (25°C, 60°C, 80°C). The observed data are shown in Table 1. The electric resistances at 80°C were about 1/2 to those observed at 25°C.

The electric resistances observed for HT/PVF membranes were two digits higher than that of the organic anion exchange membrane (Selenium AMV, Asahi Glass Co., Ltd.). The electric resistances extrapolated to 150°C which is the highest available temperature for HTs were estimated to be 37.1 – 73.4 Ω. Although as prepared membranes are not suitable to practical membranes in the electrolytic processes operated at near room temperatures, they may be practically used at higher temperature, e.g. 150°C if they are used in peculiar processes. In addition, the practical inorganic ion exchange membranes for high temperatures may be expected if the preparative conditions of membrane, e.g. decrease of the thickness of membranes due to the appropriate selection of the mixing ratio of Cl- form HT and PFV, are established properly.

The Arrhenius plots for three Cl- form HTs are shown in Fig. 6 where the abscissa indicates the reciprocal of absolute temperature and the ordinate reciprocal of the electric resistance which corresponds to the conductivity. Activation energy for the conductivity was calculated from the slope of these plots. These values are summarized in Table 2. If the electricity passed through inside the bulk hydrotalcite phase, the activation energy must be amounted to exceed at least a hundred kJ•mol⁻¹. However, calculated values were of the order of ten, and corresponded to the diffusional activation energy of ions in the solution. Therefore, it was considered that the electricity must pass through the interface.
Fig. 6 Arrhenius plots of electric conductance (inverse of resistance) for various hydrotalcite like compounds in Cl⁻ form.

Fig. 7 Membrane potential vs. log (a Na⁺) plots for HT/PVF membranes in Cl⁻ form at 25°C. :Mg-Al, :Co-Al, :Ni-Al, :Organic membrane (Selemion AMV).

Transport number was determined from the e.m.f. measurement of the concentration cell at 25°C, 60°C, and 80°C, respectively, in NaCl electrolytes. Figures 7 - 9 show the plots of the membrane potential vs. log of the activity of NaCl at each temperature. Reference solution was 0.1 M NaCl. The e.m.f. response of the HT/PVF membranes against the activity of NaCl was almost linear over the activity range of 10⁻³ - 1 M, and the transport numbers of each membrane calculated from the slopes in Figs. 7 - 9 are shown in Table 2.

Table 2 Activation energy of conductivity (inverse of resistance) for HT/PVF membranes in Cl⁻ form.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Activation energy / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al-Cl</td>
<td>14.9</td>
</tr>
<tr>
<td>Mg-Al-Cl</td>
<td>20.1</td>
</tr>
<tr>
<td>Co-Al-Cl</td>
<td>28.4</td>
</tr>
</tbody>
</table>

The slope of the line became higher with increasing the temperature and the transport number approached to 1.0 at 80°C which meant ideal anion exchange membrane. The membrane potential for the PVF membrane which contained no HT was measured for comparison. The membrane did not show any response against the activity change of NaCl. The results for the organic anion exchange membrane (Selemion AMV) measured in the similar cell is plotted in the same figure for comparison. The result indicated that the HT/PVF membranes could really act as anion exchange membranes although the available concentration range was rather narrow.

After the measurement at 80°C, the HT/PVF membranes were distorted slightly and the fact suggests that the membrane can be used at these temperature regions. However, the organic anion
exchange membrane distorted seriously and showed the weakness against the thermal resistivity.

4 Conclusion

Anion exchange membranes were successfully prepared using powdered hydrotalcite like compounds (Mg-Al-Cl, Ni-Al-Cl, Co-Al-Cl) and polyvinylidene fluoride as a binder. The membranes were dense enough and no evidence of solution leakage was observed. The electric resistances observed on HT/PVF membranes were about two digits higher than that of the organic anion exchange membrane. However, they became lower with increasing temperature. The extrapolated resistance upto 150°C was estimated to be 30–70 Ω/cm². The Arrhenius plots of HT/PVF membranes were almost linear and the values suggested that the ionic transport occurred through the surface of the hydrotalcite particles. The transport number also approached to 1.0 at 80°C, which means the formation of the ideal inorganic anion exchange membrane is possible. The thermal resistivity of inorganic HT/PVF membranes seems sufficient while organic anion exchange membrane distorted seriously during the observation at 80°C.

Table 3 Transport numbers of Cl⁻ ions for HT/PVF membranes and organic anion exchange membrane (AMV) either in Cl⁻ form.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>25°C</th>
<th>60°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Al-Cl</td>
<td>0.79</td>
<td>0.82</td>
<td>0.94</td>
</tr>
<tr>
<td>Ni-Al-Cl</td>
<td>0.85</td>
<td>0.88</td>
<td>0.94</td>
</tr>
<tr>
<td>Co-Al-Cl</td>
<td>0.86</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>AMV</td>
<td>0.85</td>
<td>0.97</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Considering the decrease in the electric resistance and the increase in the transport number with increasing temperature in addition to the thermal resistivity, it is expected that the inorganic anion exchange membrane using hydrotalcite like compounds seemed promising.

Reference

ハイドロタルサイト様化合物を用いた
無機陰イオン交換膜の研究

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要 旨

陰イオン交換性を示す無機イオン交換体を用いて陰イオン交換膜の作製を試みた。陰イオン交換体として知られているハイドロタルサイト様化合物を陰イオン導電体として、バインダーとしてポリフッ化ビニリデンを用いた。ハイドロタルサイト様化合物としては交換体の中で吸着される陰イオンの対イオンである3価イオンとしてアルニウムイオンを経通とし、主骨格を形成する2価イオンとの組み合わせとしてMg(II)-Al(III), Ni(II)-Al(III), Co(II)-Al(III)の三つの系を取り上げ、それぞれを対応する塩化物水溶液から合成した。合成したハイドロタルサイト様化合物を粉末にして、ジェチルフォルムアミドに溶解したポリフッ化ビニリデン溶液と混合後、ガラス板上で乾燥し、膜形成した。作製した膜の抵抗は0.1mol・dm⁻³ NaCl溶液中で1cm²あたり200～700Ωであった。NaCl活量1.0×10⁻²〜1.0mol・dm⁻³の範囲で電気池を形成し、塩化物イオン（Cl⁻）の輸率を計算したところ室温では0.8程度であったが、80℃ではいずれの膜も0.94と言う高い値を示し、理想的な陰イオン交換膜（有機陰イオン交換膜で0.99（実測値、室温））に近い値であった。

（9）