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Title: Anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell

Article Type: Research Paper

Keywords: poly(2,5-benzimidazole); fuel cell; anion exchange membrane; ion conductivity; thermal stability.

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Abstract: The properties of alkali doped poly(2,5-benzimidazole) membrane with different alkali doping level for fuel cell application is reported in this work. The alkali doping level played an important role for the ion conductivity of the membrane. The ion conductivity significantly increased with alkali doping level. The ion conductivity also increased with the temperature. The ion conductivity of the alkali doped ABPBI membrane (alkali doping level=0.37), reached to 2.3×10-2 S cm-1 at room temperature and 7.3×10-2 S cm-1 at 100 °C. The water uptake of the alkali doped ABPBI membrane was increased from 9.1% to 19.2% with increasing alkali doping level at room temperature. The alkali doped poly(2,5-benzimidazole) membrane also showed excellent ion conducting stability and thermal stability as compared with the known quaternized anion exchange membranes.

Dear Editor,

We would like to submit a manuscript entitled "Anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell" by Hongze Luo, Guntars Vaivars, Bolade Agboola, Mkhulu Mathe, which we wish to be considered for publication in "**Solid State Ionics**".

The aim of this work was to prepare for the first time an anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell application. The alkali doped poly(2,5-benzimidazole) membrane reached an anion conductivity of 2.3×10^{-2} S cm^{-1} at room temperature. The alkali doped poly(2,5-benzimidazole) membrane showed excellent anion conductive stability in the alkali media up to 100 °C and high thermal stability comparing with membranes based on quaternized polymers. The results suggested that alkali doped poly(2,5-benzimidazole) membrane can be a promising candidate as anion exchange membrane for fuel cell application.

We believe this study would be of interest for the researchers in fuel cell field and in a broader scientific community.

Thank you very much for your attention and consideration. We are looking forward to hearing from you soon.

Sincerely yours,

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ETHICAL STATEMENT

Title of the article: Anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell

On behalf of, and having obtained permission from all the authors, I declare that:

(a) the material has not been published in whole or in part elsewhere;

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(c) all authors have been personally and actively involved in substantive work leading to the report, and will hold themselves jointly and individually responsible for its content;

(d) all relevant ethical safeguards have been met in relation to patient or subject protection, or animal experimentation.

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Reviewer's comments to the manuscript

"Anion exchange membrane based on alkali doped poly (2,5 - benzimidazole) for fuel cell" submitted for Journal of Solid State Ionics

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Dear Editor and reviewers,

The response to reviewer's comments to the manuscript entitled "Anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell" as following,

- The accuracy of the activation energy of conductivity (Table 1) has been corrected.
- The values of ion conductivity in Fig 6 has been rewritten in correct form.
- The composition of electrolyte has been pointed out in Captions to Fig. 6 and 7.
- The TGA data of synthesized alkaline doped ABPBI membrane has been discussed comparing the literature.

The authors thank the reviewers very much for the valuable comments.

Sincerely yours,

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Anion exchange membrane based on alkali doped poly(2,5-benzimidazole) for fuel cell

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Abstract

The properties of alkali doped poly(2,5-benzimidazole) membrane with different alkali doping level for fuel cell application is reported in this work. The alkali doping level played an important role for the ion conductivity of the membrane. The ion conductivity significantly increased with alkali doping level. The ion conductivity also increased with the temperature. The ion conductivity of the alkali doped ABPBI membrane (alkali doping level=0.37), reached to 2.3×10^{-2} S cm^{-1} at room temperature and 7.3×10^{-2} S cm^{-1} at 100 °C. The water uptake of the alkali doped ABPBI membrane was increased from 9.1% to 19.2% with increasing alkali doping level at room temperature. The alkali doped poly(2,5-benzimidazole) membrane also showed excellent ion conducting stability and thermal stability as compared with the known quaternized anion exchange membranes.

Keyword: poly(2,5-benzimidazole); fuel cell; anion exchange membrane; ion conductivity; thermal stability.

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1. Introduction

Alkaline membrane fuel cell (AMFC) has recently been receiving much attention among the different types of fuel cells. The alkaline systems typically require less noble metal catalyst compared with acidic systems [1]. At the same time, they exhibit faster reaction kinetics enabling higher power densities. In alcohol fed fuel cells they can also better limit fuel cross-over and cost less than proton exchange membrane systems.

The fuel cell reaction for hydrogen fuelled AMFC is following:

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

overall: $2H_2 + O_2 \rightarrow 2H_2O$

However, the development of catalysts and membranes for AMFC is still an important issue. For example, the stability and conductivity of AMFC membranes should be improved.

Many anion exchange membranes based on quaternized polymers have been developed and studied for AMFC [2-5]. The quaternary ammonium functional groups are the anion conductors in the membranes. However, the performance of AMFC based on this type of membrane is still low due to degradation in alkaline medium at temperatures above 60 °C [6, 7]. Nevertheless, the development of anion exchange membranes for AMFC is still in the early stage [8].

Poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) is an amorphous polymer with high thermal and chemical stability. It has an excellent textile fibre property [9]. Acid doped PBI membrane was first suggested for fuel cell applications by Wainright et al. in 1995 [10]. PBI

membranes have currently been proposed as the alternative candidates for PEMFC, particularly at high temperature [11, 12].

Poly(2,5-benzimidazole) (ABPBI) is the simplest benzimidazole based polymer, which could be easily polymerized from a single commercial monomer, even without previous monomer purification. ABPBI does not contain the phenylene ring in the polymer backbone as compared to PBI. The acid doped ABPBI exhibits higher conductivity as compared to acid doped PBI, because ABPBI structure shows higher affinity towards phosphoric acid than PBI [13]. Recently, the alkali doped PBI membranes are reported as the promising candidates for AMFC application [8, 14-16]. However, the ABPBI has not been reported as the anion exchange membrane yet.

The aim of this work was to prepare the anion exchange membrane based on alkali doped ABPBI, and to investigate its properties for AMFC applications.

2. Experimental

2.1. Materials

3,4-Diaminobenzoic acid (97 %), polyphosphoric acid (85 %), formic acid (99 %) and sodium hydroxide (99 %) were supplied by Sigma-Aldrich and used without further purification.

2.2. Preparation of ABPBI membrane

ABPBI was synthesized by condensation of 6.08 g of 3,4-diaminobenzoic acid monomer in 100g of polyphosphoric acid (PPA) at 200 °C for 5 h according the procedure reported by Asensio and co-workers [17] as shown on Fig. 1.

The resulting polymer was precipitated and washed with deionised water. Subsequently, it was immersed in boiling deionised water to remove the remaining polyphosphoric acid and repeated many times until pH=7, then finally dried at 100 °C.

The ABPBI membrane was prepared by casting a solution of 1 wt% ABPBI in formic acid on a glass plate. The formic acid was evaporated overnight in a fume cupboard at room temperature. The ABPBI membrane was peeled off from the glass plate.

2.3. Alkali doping and water uptake

The membrane was doped with different concentration of NaOH solutions for various periods of time at room temperature. The alkali doping level measurements were carried out during the procedure of alkali doping. The weight gain due to the added water and NaOH was obtained by comparing the weight change before and after doping. The membrane was wiped with tissue paper, and weighed immediately. Subsequently, the membrane was dried in an oven at 150 °C until no further weight loss in order to remove the absorbed water and reweighed. The weight loss was due to the water evaporation, the water content in the alkali doped ABPBI membrane and therefore the alkali doping level could be obtained. The percentage weight loss with respect to the weight of the dried alkali doped membrane was determined as the water uptake. The value of the (weight of doped alkali)/(weight of dried ABPBI membrane) was determined as a alkali doping level.

2.4. FTIR spectroscopy

Fourier Transform Infrared **(**FTIR) spectra of ABPBI membranes were obtained in a scanning range of 600-4000 cm^{-1} on a FTIR spectrometer (PerkinElmer Spectrum™ 100).

2.5. Ion conductivity measurement

The ion conductivities were measured using electrochemical impedance spectroscopy using a (Autolab Frequency Response Analyser and poetntiostat PGSTAT30) in the frequency range from 1 Hz to 100 kHz (Fig. 2) at relative humidity 100 %. The ion conductivity σ was calculated, using following relationship:

$$\sigma = \frac{L}{RS}, \quad (1)$$

where L, R and *S* is the thickness (cm), resistance (Ohm) and contact area of the membrane (cm^2), respectively.

2.6. Morphological characterization

Hitachi X-650 scanning electron microscope (SEM) at an accelerating voltage of 25 kV was used to acquire the micrographs at the membrane cross-section after the stability test. The fragment of the membrane was mounted on aluminium stub and coated with a thin layer of gold by vacuum sputtering for three minutes.

2.7. Thermo-gravimetric analysis

The thermal stability of the membrane was analysed in a nitrogen atmosphere by using a Thermo Gravimetric Analyser (Q500) in a temperature range from 20 °C to 500 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. FTIR

The FTIR spectrum of the non-doped ABPBI membrane and the ABPBI membrane doped with 1 M NaOH for 200 h is shown in Fig. 3. The broad band at 3200-3700 cm^{-1} is assigned to the O-H vibration from molecular water. The bands characteristic for N-H stretching mode at 3250-2500 cm^{-1} are not distinguishable due to the strong absorbed water influence. A strong band at 1495-1395 cm^{-1} is attributed to the in-plane deformation of benzimidazole ring [17]. The aromatic ring has several bands at 1624, 1575 and 1430 cm^{-1}, which can be attributed to the C=N and C=C stretching [18]. The intensive band at 1409 cm^{-1} is characteristic for O-H bending mode. It is observed after doping with alkali and could be attributed to the NaOH presence.

The combination between NaOH and –NH– in the matrix of ABPBI may occur step by step via two possible ways as displayed in Fig. 4. Two possible combinations between ABPBI and NaOH can be presumed: (1) combination between Na^+ and –NH– in imidazole ring of ABPBI may occur as a result of neutralization or interaction; (2) and absorption mechanism, where hydrogen bonding between alkali OH^- and –N= in imidazole ring of ABPBI [14] is presented. The last combination is supported by FTIR spectra, because the C=N stretching modes are strongly influenced by doping. Therefore, the hydrogen bonding between alkali OH^- and –N= in imidazole ring of ABPBI is also crucial in ion transport.

3.2. Influence of doping time on doping level

The alkali doping level as a function of doping time is shown in Fig. 5. The alkali doping level initially proceeded rapidly within 50 h, but progressed slowly thereafter, which is similar to that of alkali doped PBI as reported in [14].

3.3. Water uptake and ion conductivity

The water uptake of polymer membranes is of great importance, since water is involved in electrode reactions and in transport mechanism of species in the fuel cell. The water uptake of the alkali doped ABPBI membrane at room temperature was increased from 9.1% to 19.2% with increasing alkali doping level as shown in Fig. 5. Although, the alkali doping level has little effect on the water uptake, the water uptake of the alkali doped ABPBI membrane is still sufficient to support the anion transport. At the same time, the ion conductivity of the membrane strongly depends on alkali doping level (Fig. 5). Initially, the ion conductivity of the membrane increased rapidly with increasing alkali doping level, and reaches saturation at doping level 0.3-0.4.

The value of conductivity 1.6×10^{-2} S cm^{-1} for NaOH doped PBI as measured in 1 M NaOH was reported by Xing and Svadogo's [15] and 1.8×10^{-2} S cm^{-1} by Hou et al. [8, 14]. The ion conductivity of the ABPBI membrane doped with 1 M NaOH for 200 h (doping level=0.37) is 2.3×10^{-2} S cm^{-1} at room temperature, which is higher than that reported for alkali doped PBI. It might be explained in terms of higher affinity towards alkali to ABPBI than to PBI.

It is shown on Fig. 6 that the ion conductivity of the alkali doped ABPBI membrane significantly increased with increasing temperature. The ion conductivity of alkali doped ABPBI increased from 2.3×10^{-2} S cm^{-1} to 7.3×10^{-2} S cm^{-1} in the temperature range from room temperature to 100 °C. The temperature dependence may be associated with the activation process of ion conduction in the alkali doped ABPBI membrane.

The relation between proton conductivity and temperature in general follows the Arrhenius equation. The ion transport activation energy Ea of the alkali doped ABPBI membranes was obtained using Arrhenius equation:

$$Ea=-b\times R$$

where b is the slope of the line regression of ln σ (S/cm) vs. 1000/T (K−1) plots, and R is the universal gas constant (8.31 J K-1 mol−1). The activation energy slightly decreased with the alkali doping level from 14.15 to 13.58 kJ/mol (Table 1). It demonstrates that the alkali doping enhanced the ionic mobility within these ABPBI membranes.

Table 1 Conductivity dependence on alkali doping level and temperature for alkali doped ABPBI membranes

Alkali doping level	**Conductivity** (S cm^{-1}) 20 °C 100 RH	100 °C 100 RH	**Conductivity activation energy** (KJ/mol)
0.085	1.4×10^{-2}	5.0×10^{-2}	14.2
0.24	1.9×10^{-2}	6.0×10^{-2}	13.8
0.31	2.1×10^{-2}	6.8×10^{-2}	13.8
0.37	2.3×10^{-2}	7.3×10^{-2}	13.6

The membranes based on quaternized polymers are not stable in alkaline medium at temperatures above 60 °C, therefore, the performance of AMFC based on this type of membrane is still low [6-7]. In this work, the change of ion conductivity and degradation was not observed in 1 M NaOH at room temperature and 100 °C up to 1000 h as shown in Fig. 7. It indicated that the alkali doped ABPBI membrane (ABPBI-B1000) was stable in alkali media up to 100 °C. It is expected that the usage of the alkali doped ABPBI in AMFC will improve performance and increase the working temperature range.

3.4. Thermal stability

The thermal stability of PBI has been extensively studied by thermo-gravimetric analysis [19] and the first weight loss for PBI membrane at temperatures up to 150 °C is attributed to the loss of absorbed water, typically about 13%. The doping with KOH slightly increased the water content and retention properties. The water removal was observed up to 300-400^{o}C. At temperatures over 500 °C, a significant weight loss occurs, due to the formation of carbon dioxide. We observed similar thermal behaviour for NaOH doped ABPBI membrane (ABPBI-B1000) (Fig. 8), which is suitable for fuel cell applications [20].

3.5. Morphology

The cross-section SEM image of the alkali doped ABPBI membrane is shown on Fig. 8, where dense structure is observed without porous structure presented. This is important for fuel cell applications, where porous structure might increase the fuel permeability.

Conclusions

The investigated ABPBI membranes after doping with NaOH exhibited high ion conductivity, which increased with the doping level. The thermal and chemical stability of alkali doped ABPBI membrane in the alkali media was observed up to 100 °C, which is better performance as compared to the known quaternized anion exchange membrane.

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Figure captions

Fig. 1. Synthesis of ABPBI.

Fig. 2. Schematic view of conductivity cell.

Fig. 3. FTIR spectra of ABPBI membranes.

Fig. 4. Micro-structure of alkali doped ABPBI membrane.

Fig. 5. Alkali doping level vs. doping time and water uptake and ion conductivity vs. alkali doping level.

Fig. 6. Ion conductivity in 1 M NaOH vs. temperature and the ln σ vs. 1000/T plot.

Fig. 7. Ion conductivities in 1 M NaOH of alkali doped ABPBI membrane.

Fig. 8. TGA and SEM of alkali doped ABPBI membrane.

***Research Highlights**

In the present manuscript the preparation and the characterization, for fuel cell application, of a poly(2,5-benzimidazole), doped with alkali (NaOH) has been investigated for the first time. There is no similar work reposted in the literature. The alkali doping level played an important role for the ions conducting through the membrane. The ionic conductivity of the membrane increased with alkali doping level. The alkali doped poly(2,5-benzimidazole) membrane reached an anion conductivity of 2.3×10^{-2} S cm^{-1} at room temperature. The alkali doped poly(2,5-benzimidazole) membrane showed excellent anion conductive stability in the alkali media up to 100 °C and high thermal stability comparing with membranes based on quaternized polymers.

We believe this study would be of interest for the researchers in fuel cell field and in a broader scientific community.

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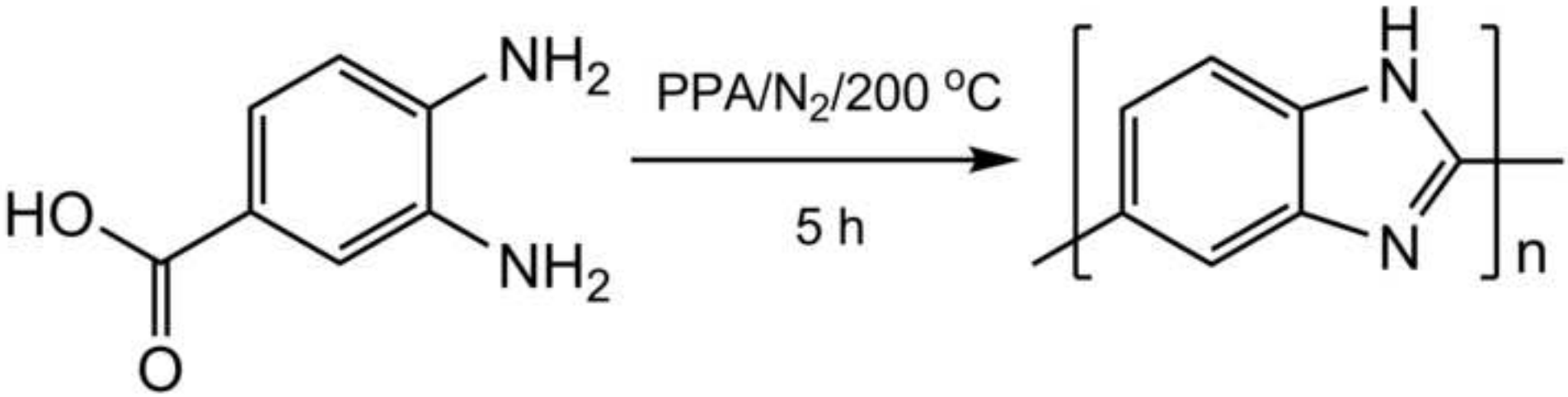

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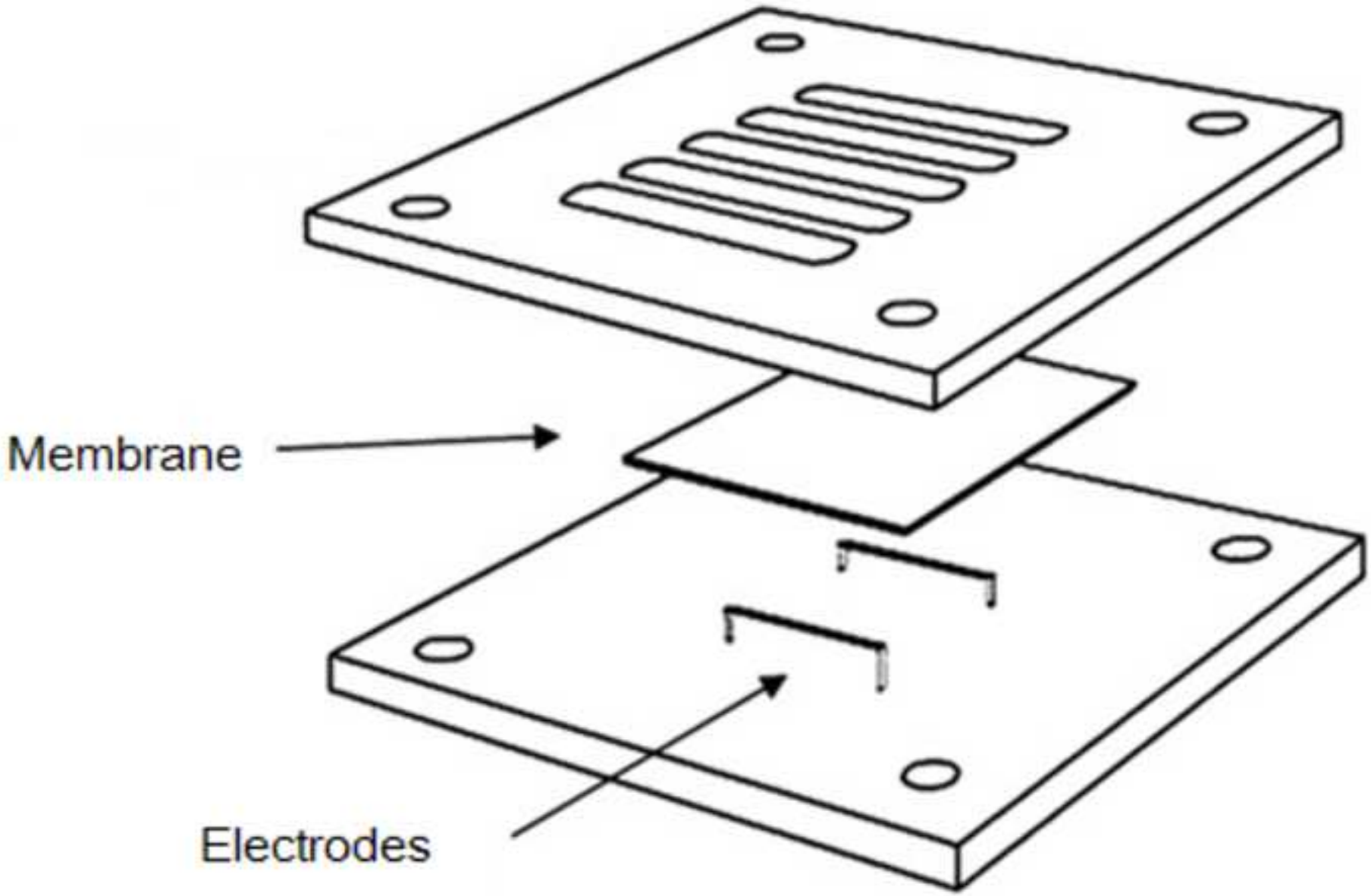

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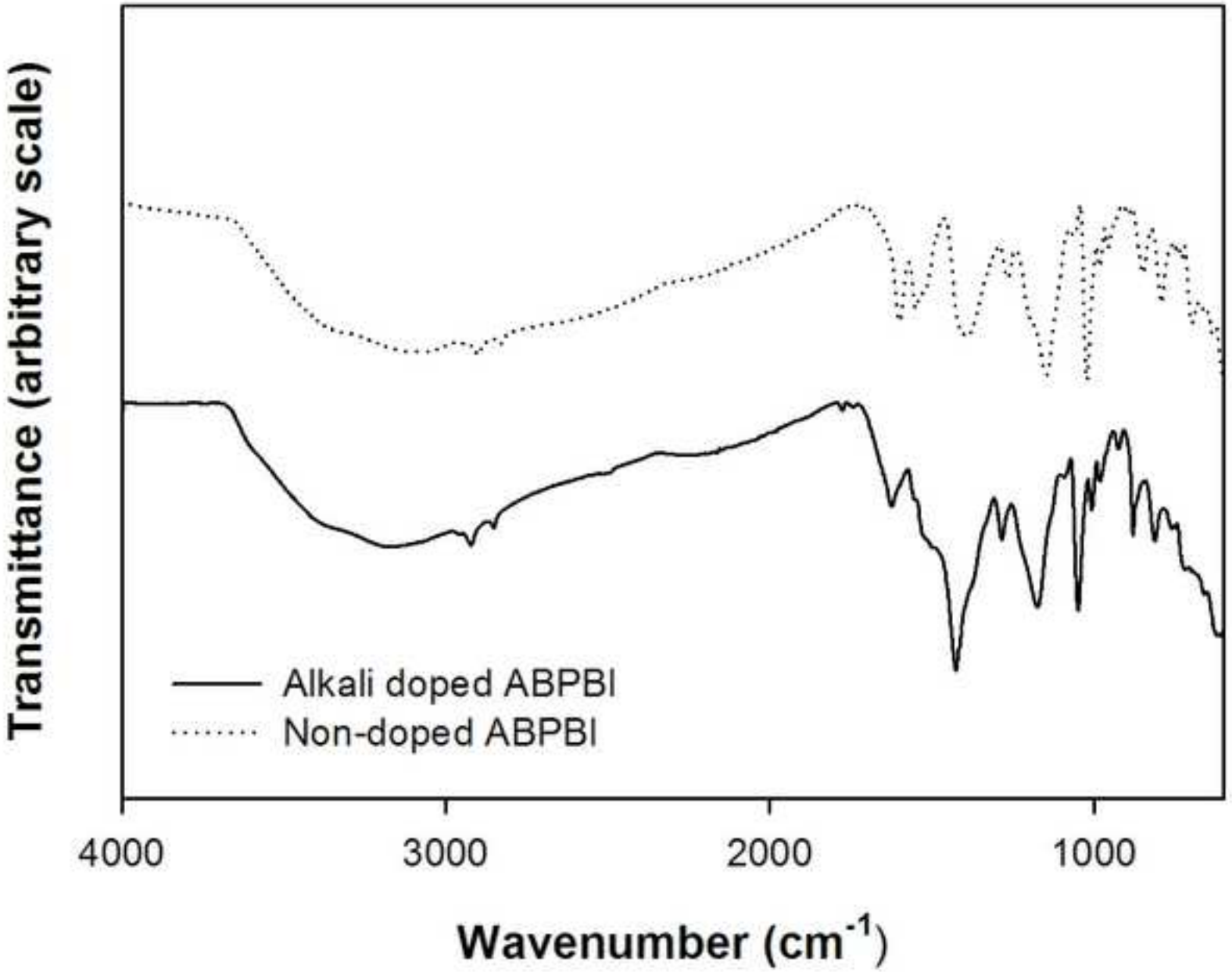

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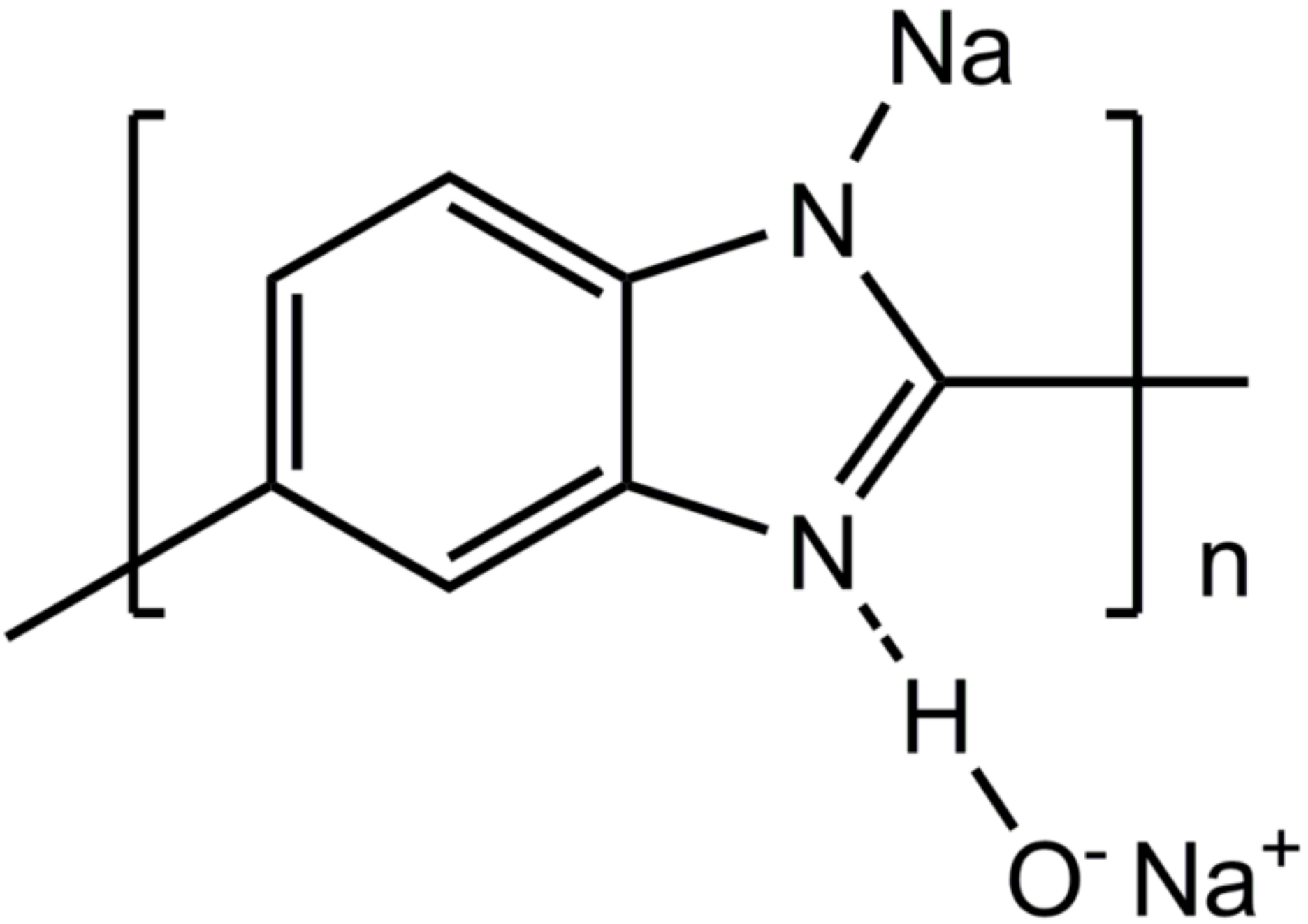

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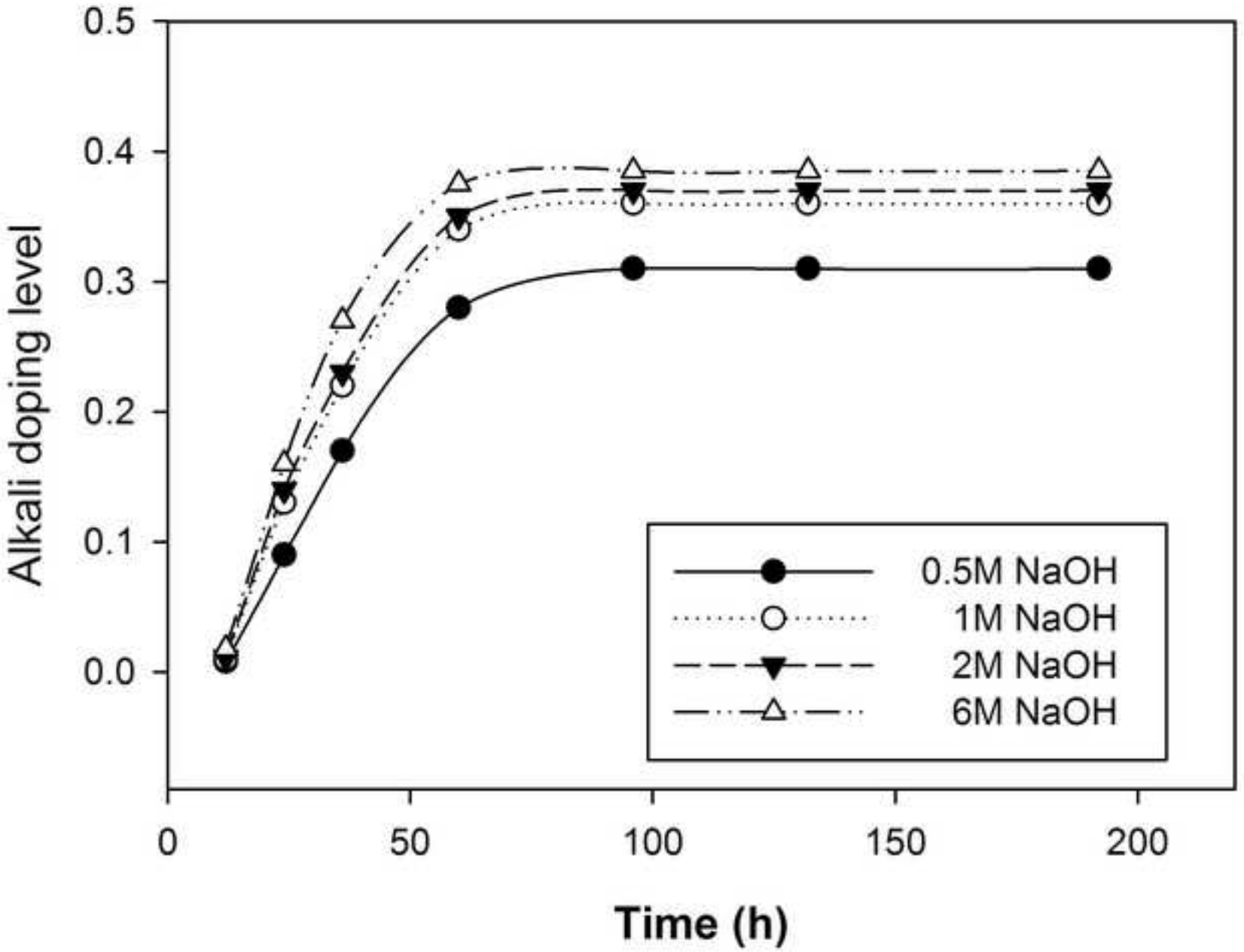

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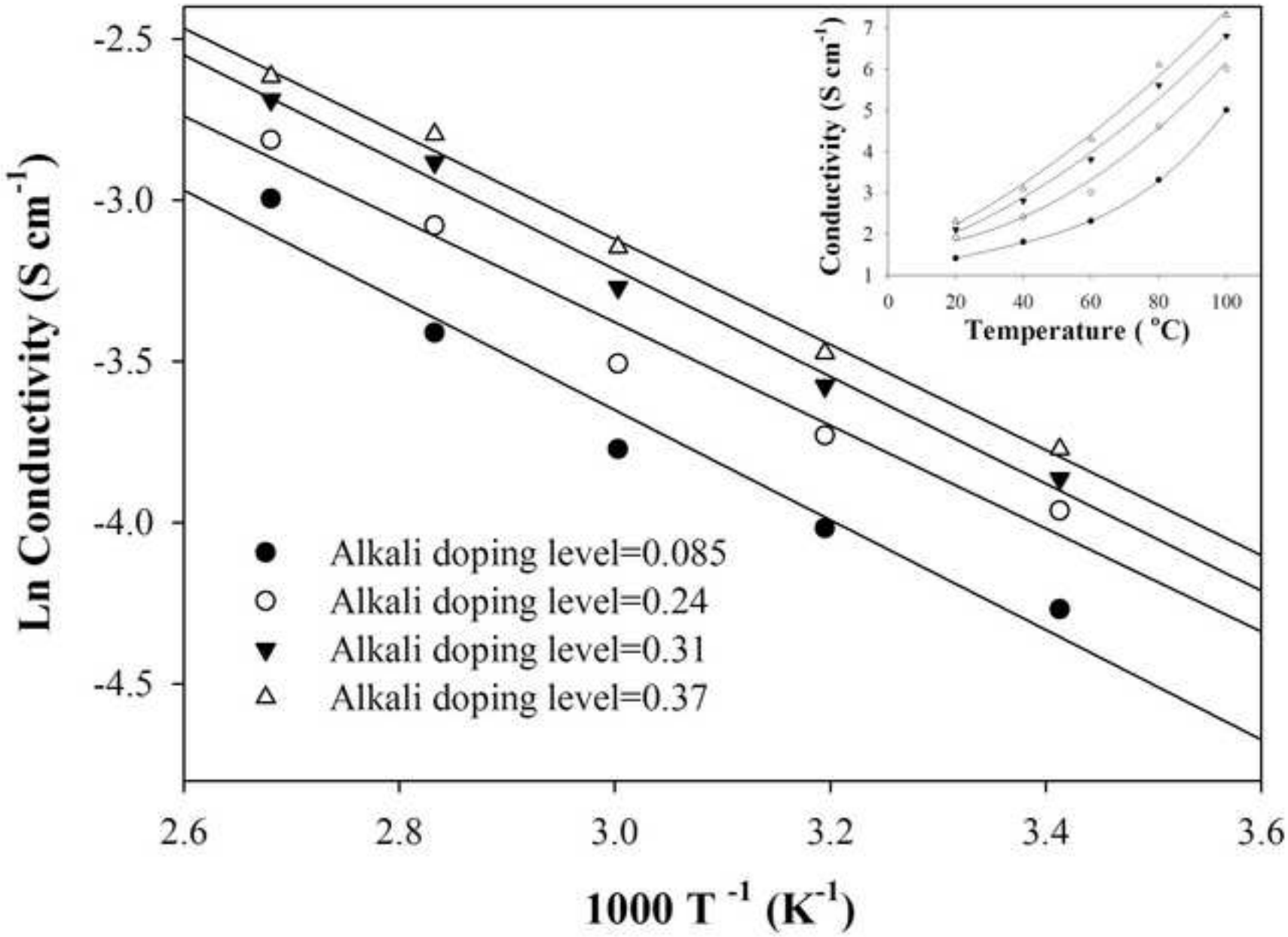

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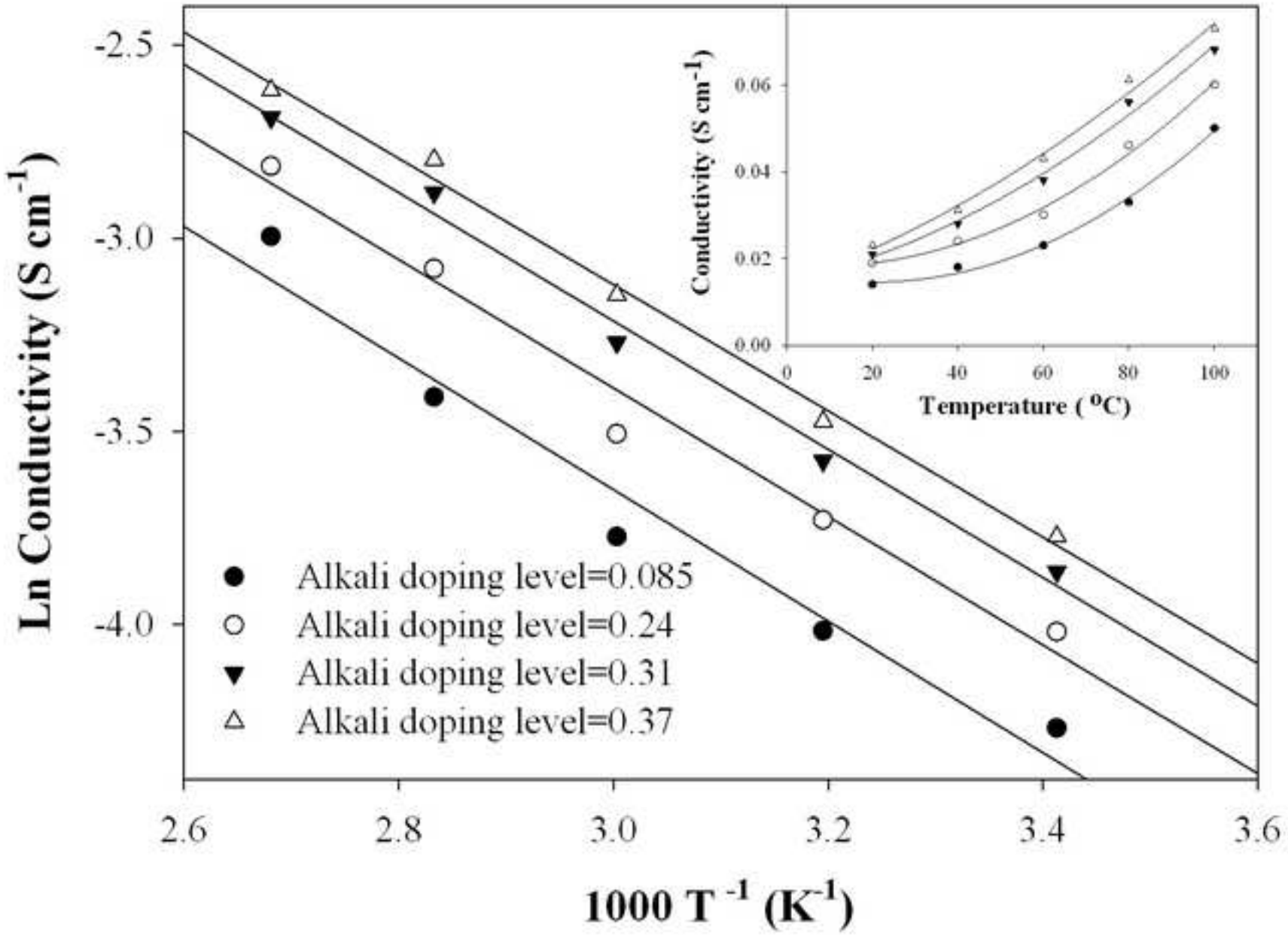

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