



Short communication

Durability study of KOH doped polybenzimidazole membrane for air-breathing alkaline direct ethanol fuel cell

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ABSTRACT

Recently, KOH doped polybenzimidazole (PBI/KOH) membrane has been reported as polymer electrolyte membrane for alkaline direct alcohol fuel cell (ADAFC), but little is known about its durability for ADAFC application. In this paper, the durability of PBI/KOH membrane for air-breathing alkaline direct ethanol fuel cell (ADEFC) is evaluated by means of ex situ and in situ tests. In the case of ex situ durability test, the ionic conductivity of PBI/KOH degrades from initial 0.023 S cm^{-1} to 0.01 S cm^{-1} after 100 h, and the degrading rate was $1.3 \times 10^{-4} \text{ S cm}^{-1} \text{ h}^{-1}$. As for in situ test, Pt-free air-breathing ADEFC with PBI/KOH membrane can output a peak power density of 16 mW cm^{-2} at 60°C . Moreover, it can stably operate for 336 h above 0.3 V. In addition, the interaction between KOH and PBI matrix is also explored by density functional theory study.

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1. Introduction

In recent years, alkaline direct alcohol fuel cell (ADAFC) has become a new focus due to faster electrochemical reaction kinetics in alkaline medium than in acid medium [1–6]. In ADAFC, ethanol is a preferred fuel because of its non-toxicity and less carbonation effect in the electrode [7–9]. As one of the key components, alkaline polymer electrolyte membrane plays an important role in the performance and durability of ADAFC. However, the challenges still exist in the development of stable anion exchange membranes. Therefore, the corresponding study becomes more and more attractive.

As one kind of organic base, quaternized polymer is an anion exchange membrane. Generally speaking, it is composed of three parts: (i) the polymer backbone; (ii) the functional group with positive charge ($-\text{NR}^4+$ or $-\text{PR}^4+$); and (iii) the movable anion on the functional group, as shown in Fig. 1. Therefore, quaternized polymer can selectively allow the passage of the anion but reject the cation. It was developed prior to ADAFC and applied widely in many fields such as salt electro dialysis [10], anion selective electrode [11], recovery of waste organic acids [12] and batteries [13]. Recently, increasing efforts have been made to study its application

in ADAFC [1,4,14,15]. Up to now, there have been two kinds of commercial quaternary anion exchange membranes (Morgane[®]-ADP in Belgium and Tokuyama[®] in Japan) for ADAFC application [5,16,17]. And active ADAFC with Tokuyama[®] as electrolyte membrane can deliver a peak power density of 60 mW cm^{-2} at 40°C [8]. Unfortunately, the quaternized group is unstable in concentrated alkaline medium above 60°C due to nucleophilic displacement or Hoffman elimination reaction [18], which limit its wide application for ADAFC. As mentioned above, although some primary achievements about alkaline polymer electrolyte membrane for ADAFC have been made, the corresponding study is still far away from maturity compared with that of proton exchange membrane. Therefore, it is very necessary to carry out further investigation.

Polybenzimidazole (PBI) membrane is well known for its excellent endurance in alkaline medium, and it can become an ionic conductor when doped with inorganic hydroxides [19]. Therefore, in our previous work, KOH doped PBI membrane for ADAFC was evaluated at 90°C , and the corresponding performances of ADAFC were improved possibly due to fast dynamics even if the concentration of KOH was only 2 M [20,21]. However, up to now, there are fewer reports about the durability study of ADAFC with PBI/KOH as electrolyte membrane. In this paper, in order to further gain the insight into the durability and degradation of PBI/KOH as an electrolyte membrane, ex situ and in situ durability studies of PBI/KOH for air-breathing alkaline direct ethanol fuel cell (ADEFC) were designed and performed. In addition, the interaction between KOH and PBI matrix was also further explored by density functional theory (DFT) study.

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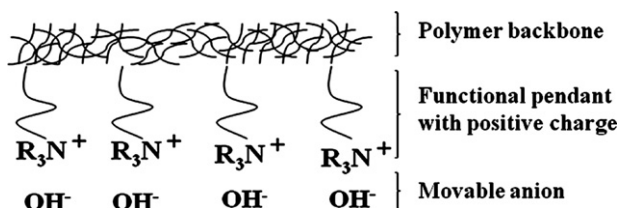


Fig. 1. Schematic microstructure of wet quaternized anion exchange membrane.

2. Experimental

2.1. Materials

PBI film was friendly supplied by our cooperator. It possessed the same micro-structure as the commercial one, and its thickness was about 50 μm . Potassium hydroxide pellet was used as received without being purified.

2.2. Ex situ durability test of PBI/KOH membrane

Ex situ durability test of PBI/KOH membrane was performed by consecutively monitoring its ionic conductivity at room temperature for 100 h. Prior to measuring the ionic conductivity, the sample was washed with deionized (D.I.) water for several times in order to remove KOH on the surface of the membrane. It was then sandwiched between two Teflon plates with platinum wires as the electrodes. During the experiment, the setup was put into a beaker with D.I. water. Moreover, D.I. water was updated before every measurement. The ionic conductivity of PBI/KOH was measured on the potentiostat (CHI760) from 100 mHz to 100 kHz with oscillating voltage of 10 mV.

2.3. In situ durability test of PBI/KOH membrane for air-breathing ADEFC

45% PtRu/C (purchased from Johnson Matthey Inc.) or 40% Pd/C (homemade by method of sodium borohydride reduction) were used as anode catalysts. Cathode catalyst, 40% MnO_2/C was prepared by method of liquid phase deposition. The loadings of PtRu or Pd at the anodes and of MnO_2 at the cathode were 2.0 and 1.0 mg cm^{-2} , respectively. Nafion[®] ionomer was incorporated into the electrodes as binder, and the loading of ionomer was about 1.0 mg cm^{-2} . The membrane and electrode assembly (MEA) was prepared by sandwiching PBI/KOH membrane between two electrodes. It was then placed between two stainless steel plates with channels to form a single cell with an active area of 4 cm^2 . Single cell tests were performed at 60 °C using a commercial fuel cell test system (Arbin Instrument Corporation). 2 M KOH was fed into the anode along with 2 M ethanol at a flow rate of 1 mL min^{-1} in order to establish three-phase boundary, while the oxidant was supplied by self-diffusion of the air in the atmosphere. The in situ durability test of air-breathing ADEFC with PBI/KOH membrane was performed at 60 °C by constant current density (25 mA cm^{-2}) discharge.

3. Results and discussion

3.1. Ex situ durability test of PBI/KOH membrane

Generally speaking, a desired polymer electrolyte membrane for ADEFC should have enough ionic conductivity. Otherwise, ADEFC cannot deliver electric power due to large internal resistance. Therefore, the ionic conductivity is a very important parameter. In this work, the ex situ durability of PBI/KOH membrane was investigated by monitoring its ionic conductivity at room temperature for

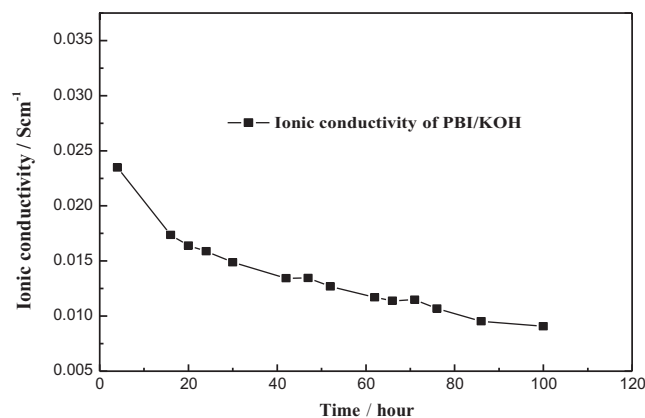


Fig. 2. The curve of the ionic conductivity of PBI/KOH as a function of the time.

100 h. As shown in Fig. 2, the initial ionic conductivity of PBI/KOH membrane was 0.023 S cm^{-1} , which was acceptable compared to those of other anion exchange membranes in literatures [6,22]. Thereafter, the ionic conductivity of PBI/KOH membrane slowly degraded with the test time. After 100 h, the ionic conductivity of PBI/KOH decreased from initial 0.023 to 0.01 S cm^{-1} , and the degrading rate was $1.3 \times 10^{-4} \text{ S cm}^{-1} \text{ h}^{-1}$.

3.2. In situ durability test of PBI/KOH membrane for air-breathing ADEFC

As mentioned above, ex situ durability test is usually used to evaluate the endurance of the membrane in terms of the partial property. The final durability of the membrane must be confirmed by in situ test under the operation conditions of fuel cell. Therefore, in order to obtain further durable information of PBI/KOH, in situ durability experiment was also designed by assembling single cell with PBI/KOH as an electrolyte membrane. In addition, in order to simulate the operation conditions of ADEFC for portable devices, self-diffusion of the air is a preferred supply mode of the oxidant.

As shown in Fig. 3, in situ durability test of PBI/KOH for air-breathing ADEFC was performed at 60 °C, with 45% PtRu/C and 40% MnO_2/C as anode and cathode catalysts, respectively. It can be seen that the lifetime of air breathing ADEFC with PBI/KOH was about 256 h. In addition, although the voltage of air-breathing ADEFC was automatically fluctuated, the center of the voltage fluctuation was

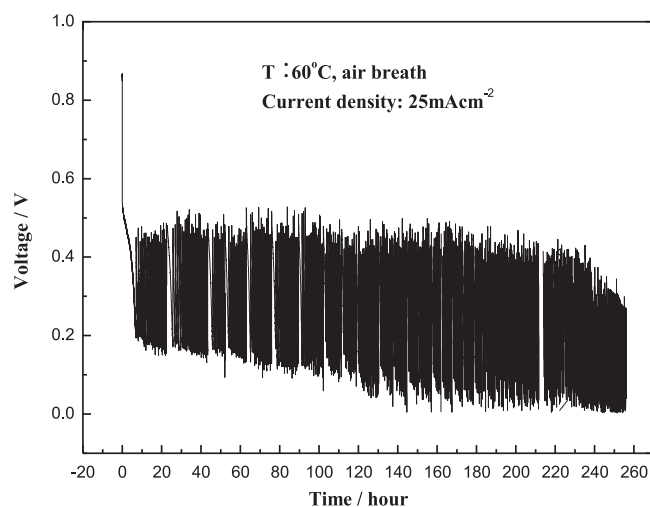


Fig. 3. The lifetime of air breath ADEFC with PBI/KOH at 60 °C, anode catalyst: 45% PtRu/C, cathode catalyst: 40% MnO_2/C , constant current density: 25 mA cm^{-2} .

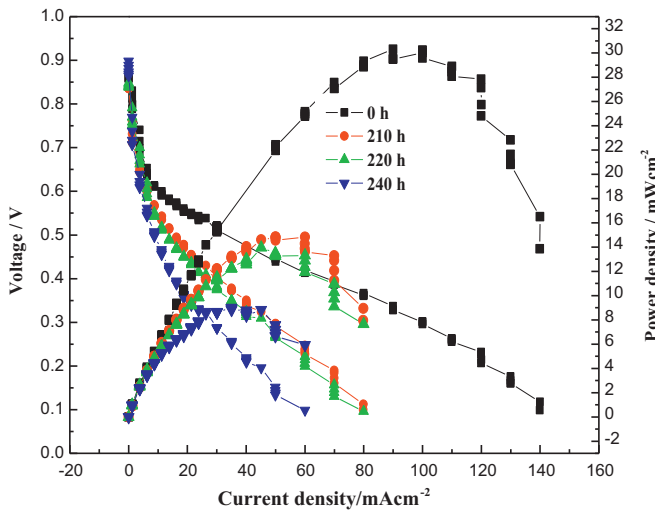


Fig. 4. The performances of air breath ADEFC with PBI/KOH at 60 °C, anode catalyst: 45% PtRu/C, cathode catalyst: 40% MnO₂/C.

almost constant (0.3 V) within 100 h and then slowly degraded to 0.2 V within the rest 156 h. During the experiment, the i - V and i - P curves were collected at 0 h, 210 h, 220 h and 240 h, respectively, as shown in Fig. 4. The corresponding peak power densities were about 30 mW cm⁻², 15 mW cm⁻², 14 mW cm⁻² and 9 mW cm⁻², respectively. According to the power densities at different times, the degrading rate can be calculated to be 0.08 mW cm⁻² h⁻¹. It is noteworthy that the initial power density of 30 mW cm⁻² is satisfying and higher than some results of active ADEFC in literatures [4,23], even close to that of active ADEFC at the same temperature (60 °C) [7].

In order to explore the possible reason for the voltage fluctuation, anode catalyst of 45% PtRu/C was changed into 40% Pd/C, while other conditions were identical. The V - t curve of the resulting ADEFC was shown in Fig. 5. To be satisfying, the obtained air-breathing ADEFC can stably operate for 336 h without obvious voltage fluctuation, which was much better than that of traditional alkaline fuel cell with KOH solution as electrolyte. It was reported that the performance of traditional alkaline fuel cell rapidly degraded after 70 h at 60 °C and 94 h at 30 °C due to carbonate precipitation at the anode, when fuelled with methanol [24]. Likewise, the i - V and i - P curves of air-breathing ADEFC at different times were also obtained, as shown in Fig. 6. The peak

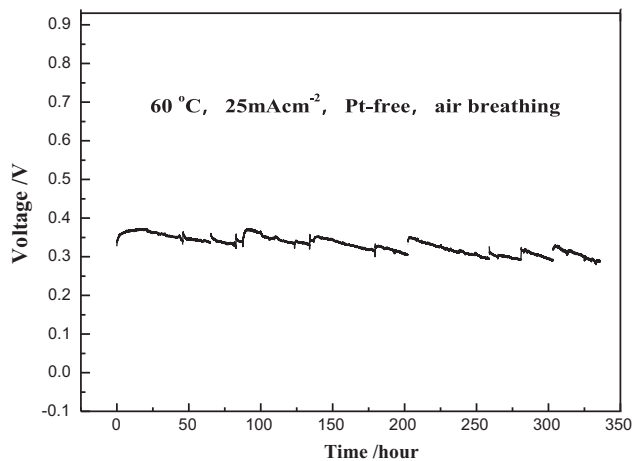


Fig. 5. The lifetime of air breath ADEFC with PBI/KOH at 60 °C, anode catalyst: 40%Pd/C, cathode catalyst: 40% MnO₂/C, constant current density: 25 mA cm⁻².

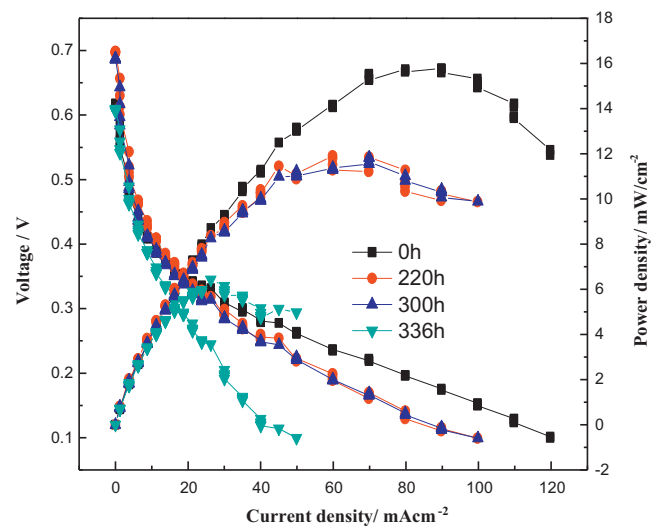


Fig. 6. The performances of air breath ADEFC with PBI/KOH as an electrolyte membrane at 60 °C, anode catalyst: 40% Pd/C, cathode catalyst: 40% MnO₂/C.

power densities at 0 h, 220 h, 300 h and 336 h were 16 mW cm⁻², 12 mW cm⁻², 12 mW cm⁻² and 7 mW cm⁻², respectively. According to these results, the degrading rates in terms of the peak power density within 300 h and within 336 h can be calculated to be 0.013 and 0.027 mW cm⁻² h⁻¹, respectively. The degrading rates especially within 300 h were much lower than that of air-breathing ADEFC with 40% PtRu/C as anode catalyst (Fig. 7). By comparing the performances of two air-breathing ADEFCs, one can find that there was a compromise between the power density and the durability of ADEFC when 40% Pd/C was used as anode catalyst.

3.3. Discussion

As mentioned above, the ex situ durability of PBI/KOH was evaluated by monitoring its ionic conductivity for 100 h. The degrading rate was 1.3×10^{-4} S cm⁻¹ h⁻¹, that is, the ionic conductivity of PBI/KOH did not rapidly degrade in a very short time. This durability result implied that KOH may be anchored within the backbone of PBI to some degree by weak chemical bonds, which can be also supported by SEM-EDX result [20]. In this literature, two possible combinations were presumed between PBI and KOH: one is the

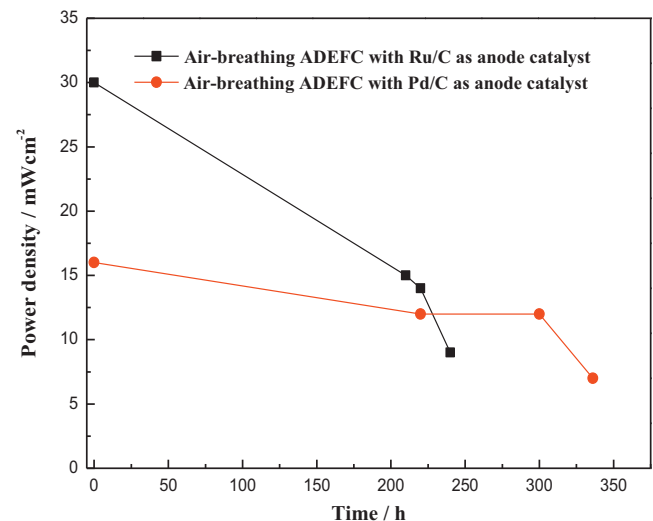


Fig. 7. The curves of the peak power density as a function of the time.

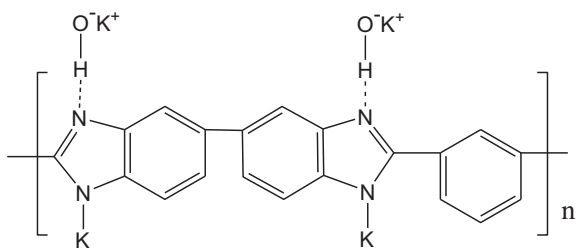


Fig. 8. The scheme of combination between KOH and PBI matrix.

combination between K^+ and $-NH-$ in PBI matrix as a result of a neutralization between H in $-NH-$ and OH^- in the medium; the other is hydrogen bond between OH^- and $-N=$ in the backbone of PBI, with K^+ as counter ion, as shown in Fig. 8. Here, in order to further explore the possibility of the interaction between KOH and the backbone of PBI, the bond lengths and the bond energies of N–K and N–H were calculated according to DFT. As shown in Fig. 9, the bond length and the bond energy of N–K were 2.1009 Å and 1.7215 eV, respectively, indicating the feasibility of combination between N and K. In the case of N–H, the bond length and the bond energy were 1.042 Å and 4.2785 eV, respectively. Compared with N–H, N–K had larger bond length and smaller bond energy. This implied that in principle, it is difficult that K^+ automatically displace H^+ in $-N-H$ without any exterior help. However, it did not indicate that K^+ cannot passively displace H^+ with exterior help. In this work, OH^- may act as the role of exterior help and make this passive displacement possible. As shown in Fig. 10, a possible mechanism is as follows: (i) $-N-H$ can dissociate into H^+ and $-N^-$, which is a very weak balance reaction and can be verified by reaction between PBI and LiH [25]; (ii) the resulted H^+ can combine with OH^- in the medium to form more stable H_2O , which makes this balance shift to the right; and (iii) in order to maintain the charge balance, K^+ in the solution must combine with $-N^-$ to form $-N-K$. This possible mechanism can be also supported by SEM-EDX results, in which the concentration of K element within PBI was much higher than that of O element in spite of the possible incorporation of H_2O and CO_2 in the air [19]. Conversely, the combination of K^+ with $-N^-$ in PBI matrix and the departure of OH^- as form of H_2O can reasonably explain SEM-EDX result.

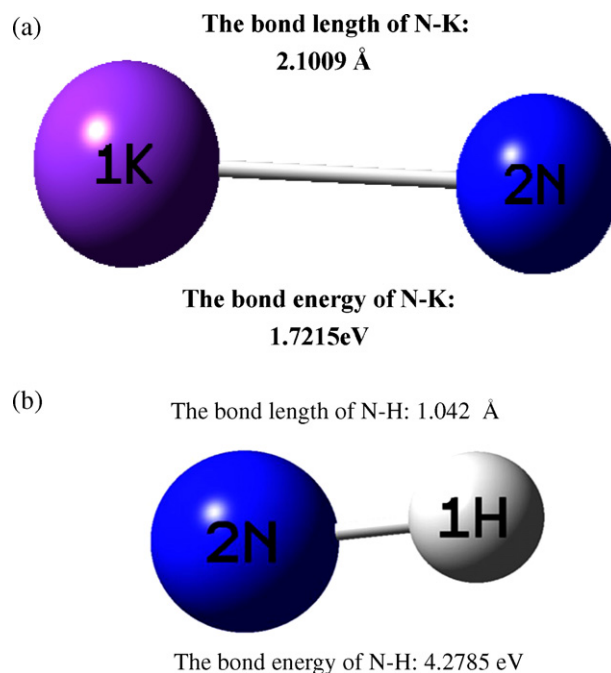


Fig. 9. The bond lengths and bond energies of N–K (a) and N–H (b) calculated by DFT.

Ex situ assessment provided the evidence that KOH may be anchored by weak chemical bond within PBI matrix, while it failed to provide the durable information of PBI/KOH as an electrolyte membrane for air-breathing ADEFC. Therefore, two in situ durability tests were also designed. Firstly, an air breathing ADEFC was assembled, in which PBI/KOH was employed as electrolyte membrane, 45% PtRu/C as anode catalyst, and 40% MnO_2/C as cathode catalyst. The lifetime of ADEFC was about 256 h with automatic voltage fluctuation. In order to explore the possible reason for the voltage fluctuation, another experiment was also performed, in which 45% PtRu/C was replaced by 40% Pd/C, while other conditions was unchanged. It can be found that the durability of the second air-breathing ADEFC was greatly improved without obvious voltage fluctuation even under the same operation conditions. Therefore, it is presumed that the reason for the voltage fluctuation should

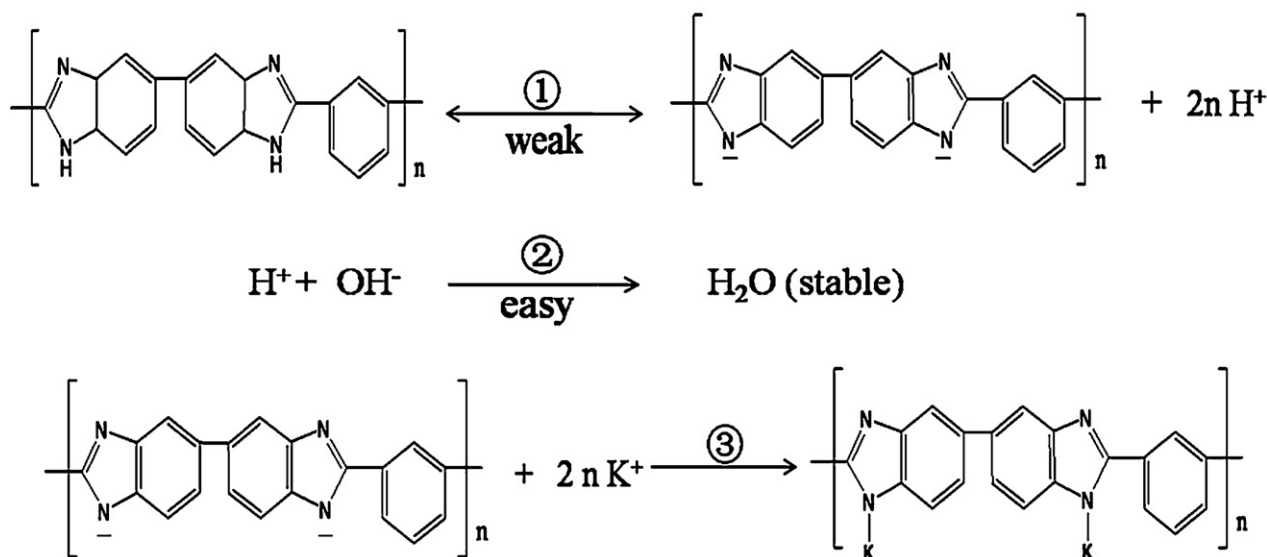


Fig. 10. The possible combination mechanism of N–K bond.

not be from PBI/KOH membrane but from PtRu/C catalyst. There was no doubt that as one of the key components of air-breathing ADEFC, PBI/KOH membrane played an important role in the stable operation of ADEFC during the test time. It was also reported that Pd was a good electrocatalyst for ethanol electro-oxidation reaction in alkaline medium, with better steady-state behavior than Pt-based catalyst [26], which also facilitated the stable operation of ADEFC. For 45% PtRu/C catalyst, the detailed reason for the voltage fluctuation is not sure yet, and will be explored in the next work. From the power density degrading rate of the second air-breathing ADEFC (see Fig. 7), it can be judged that the degradation of ADEFC within 300 h is much slower than that during the last 36 h. The reason may be lie in the precipitation of acid product from ethanol electro-oxidation, and the precipitation may slowly collapse the triple-phase structure within the electrode, especially during the last 36 h [21]. It was reported that the negative effect of carbonation can be alleviated to some degree by using ethanol as fuel, because the cleavage of the C–C bond in ethanol molecule cannot easily take place under mild conditions [9]. However, this negative effect of the precipitation cannot be avoided completely yet. Therefore, the control of ethanol electro-oxidation and alleviation of the precipitation effect may be effective strategies to improve the lifetime of ADEFC. In addition, the durability results of PBI/KOH membrane for several hundred hours still fail to provide enough information about long-term durability of PBI/KOH for ADEFC. Compared to Nafion® membrane for acid DAFC, the decays in ionic conductivity and cell performance are still serious. However, these results can provide the primary feasibility about the durability of PBI/KOH. Further improvement may be achieved by sustaining efforts in the future.

4. Conclusions

The durability of PBI/KOH membrane for air-breathing ADEFC was evaluated by means of ex situ and in situ tests, and some primary durability results of PBI/KOH membrane were obtained. The ionic conductivity of PBI/KOH decreased from initial 0.023 S cm^{-1} to 0.01 S cm^{-1} after 100 h, and the degrading rate was $1.3 \times 10^{-4} \text{ S cm}^{-1} \text{ h}^{-1}$. At 60°C , Pt-free air-breathing ADEFC with

PBI/KOH as electrolyte membrane can stably operate for at least 336 h above 0.3 V. Although the durability of 336 h is not very long, the preliminary results are inspiring, indicating the feasibility of PBI/KOH for ADEFC application.

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