

A Polymer Membrane for Water Electrolysis in Alkaline Solutions

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A kind of linear polymer containing crown ether group was synthesized and the membrane was made of the polymer. A special process treatment made the membrane can transport the ion and can be used for the water electrolysis in alkaline solutions. The characterization of the membrane such as the tensile strength test, SEM and XRD was examined and the performance of the electrolysis cell was also tested. The resistance of the membrane is $0.23 \Omega \text{ cm}^2$; the cell voltage is lower than 2.0 V (25 °C, 5 mol/L KOH, 200 mA/cm²).

Keywords: Membrane, Water electrolysis, Crown ether.

INTRODUCTION

Since the crises of fossil fuels increase and in order to protect the environment, the present energies, *i.e.*, petroleum, coal and natural gases will be substituted by other clean energies such as solar energy, wind energy and hydrogen energy. Amongst these new energies, hydrogen is an ideal one because of no pollution, easy to store and abundant sources. Hydrogen energy and electric energy will be the most important ones in the energy system¹. Hydrogen production *via* electrolysis of water from alkaline aqueous electrolytes is a well-established conventional technology. Hydrogen's energetic potential lies in its ability to serve as recent technology progress makes hydrogen a realistic energy option. It is a long-term energy option, which means one of "fuels of the future" for buildings, transportation, portable application, vehicles and propellant for space mission, *etc.* Hydrogen can be used as a storage medium for intermittent and seasonal renewable technologies². The project of electrolysis of water certainly needs septum to separate the hydrogen and oxygen.

At present the commonly septum material in an electrolysis cell is mineral ultrafiltration membranes such as asbestos membrane³ (in alkaline solutions) and solid polymer electrolyte (SPE) membrane such as Nafion or Flemion^{4,5} (in acid solutions or alkaline solutions). The mechanism of ion transmission is different between the SPE membrane and the asbestos membrane. There are respective advantages and shortcomings between the two kinds of membranes. For example, asbestos membrane has been forbidden to use in many developed countries because it is a kind of carcinogen to be proved though

the electrochemistry performance is excellent. The SPE membrane such as Nafion or Flemion showed a better electrochemistry performance when it was using for water electrolysis in acid solutions than alkaline solutions because the transferred velocity of proton is quicker than the other ions. But, generally, the erosion to devices is serious under acid conditions. Further more, the high price of Nafion or Flemion membrane limited their uses in many occasions, though its steady structure consist of fluorinated chains. In some countries, the low-cost SPE membrane has been investigated to substitute for Nafion or Flemion⁶. Another idea that to find polymers to substitute for mineral ultrafiltration membranes such as asbestos membrane has been suggested because there are more advantages of water electrolysis in alkaline solutions than in acidic solutions. Our groups put out a proposal that a membrane made of a kind of polymer containing crown ether groups was applied to water electrolysis.

Since macrocyclic polyethers were discovered by Pederson⁷, they have enjoyed a considerable interest during the past years because their chelation properties to metal ions and a quite great progress has been made by the scientists from all over the world. Some linear polymers containing crown ether groups were synthesized and characterized⁸. For example, a membrane based macrocyclic polyether-polyamide was applied to osmotic membrane and hyperfiltration membrane⁹. The polymers containing crown ether groups can chelated metal ions and convey ion like mono-molecule crown ether while they have a less toxicity than mono-molecule crown ether¹⁰.

The ion can transfer through the membrane according to the method of chelation of crown ether groups. So a new idea

that a membrane was made of the polymer containing crown ether group and applied to water electrolysis was put forward by our research groups.

EXPERIMENTAL

The dibenzo-18-crown-6 (Aldrich, m.p. 161-163 °C) was dried overnight under 130 °C. The sebacic acid (The Second Reagent Factory, Tianjin) was dried under vacuum overnight in 70 °C. The polyphosphoric acid (PPA) (80 %) (Chemistry Reagent Factory, Shanghai) and the other solvents (such as chloroform) were used without further purification. The electrode materials were activated Raney Ni alloys that supported by our laboratory.

Preparation of linear polymer containing crown ether group: The high molecular weight polymer containing crown ether group was synthesized according to the reported method¹¹. The reaction and the structure of the polymer is as shown in Fig. 1.

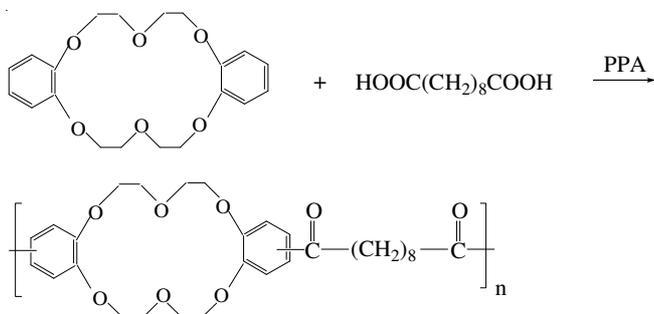


Fig. 1. Reaction and the structure of the polymer containing crown ether group

Ketonic type polymer was obtained by acylating dibenzo-18-crown-6 with sebacic acid in polyphosphoric acid under 60 °C after 6 h. From the structure of the polymer, the crown ether group lies in the main chain of the polymer. The hydrophilic property and the chelate capability to metal ions are not as good as the polymer that the crown ether group lies in the side chains^{12,13}. On the other hand, it should have good heat-resistant property because of two phenyl rings in each unit of the polymer main chains. And a good heat-resistant property is necessary for the membrane to electrolyze water.

Preparation of membrane and the treatment to the membrane: The solution of dissolved copolymer containing crown ether group (1 g) in 15 mL chloroform was cast on a glass gasket and the chloroform allowed to evaporate at room temperature with a good aerator. The membrane was dislodged carefully. Dried membrane (MA) of thickness 75 μm was obtained.

The membrane then dipped into a mixed saturated solution. The mixed solution consists of isopropanol, methanol, deionized water and saturated KOH. The process lasted some hours. Then the membrane was taken out from the solution and washed by methanol and deionized water. The membrane being treated (MB) can be applied to the electrolysis cell.

The membrane treated was applied to the electrolysis cell. The constant-current charge density is 200 mA/cm². The membrane after water electrolysis in KOH solutions (MC) was examined some other properties. MA, MB and MC were

characterized by tensile strength test, XRD, SEM and then they were compared.

Characterization of membrane: The tensile strength and breaking elongation of the membranes were measured on an electron tensile tester (XINSANSI-cmt6202, Shenzhen) with a tensile rate of 5 mm/min, at a gauge length of 50 mm and width of 10 mm. The temperature and relative humidity were 25 °C and 60 %, respectively. The Wide-angle X-ray diffraction (XRD), patterns of the membranes of 75 μm thickness were recorded with a Shimadzu XRD-6000 (Japan) diffractometer by using a Cu K_α target at 40 KV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 5-45°. The morphology of membranes surfaces was examined by a Hitachi-570 scanning electron microscope (Japan). The membranes were frozen under liquid nitrogen to fracture and were coated with gold under 13.3 Pa vacuum conditions before the SEM experiments. The ionic resistance of membrane was tested by the battery testing system (XinWei Company, Ltd., Shenzhen, China).

RESULTS AND DISCUSSION

Mechanical properties of membrane: The mechanical properties of membranes are very important for its applications. The mechanical performances of the membrane are shown in Table-1. From Table-1, an obvious order can be observed, MA > MB > MC in each performance. From the order of the thickness of MA > MB > MC, the conclusion can be drawn that there is something lost when the MA dipped into the mixed solutions. A reasonable explanation is that the solubility of MA in mixed solution is better than the ones in water. It is well known that the crown ether group can chelated the alkali metals ions⁷. And the log K (K = [chelated matter]/([crown ether]·[alkali metals ions])) (K is the equilibrium constant) is higher in methanol than in water¹⁴. For the polymer containing crown ether group, a hydrophobic surface made the MA couldn't conduct. When the mixed solutions added, the polymer containing crown ether group can chelate K⁺ in mixed solutions and some segment of the polymer dissolved. log K of the 18-crown-6 is the maximal to that of K⁺ because the diameter of K⁺ (2.66 ⊕) is close to the diameter of 18-crown-6 (2.6-3.2 ⊕)¹⁵. Thus, we choose the K⁺ as the caught ion. There is a part of polymer dissolved in the mixed solutions. This is due to the reason of the thickness of MA > MB > MC. And therefore the hole formed. The mechanical properties of membrane descended are logical according to the order MC < MB < MA because of the hole existing.

TABLE-1
MECHANICAL PERFORMANCE OF MEMBRANES

	Thickness (mm)	Tensile strength (M Pa)	Elongation at break (%)	Elastic modulus (M Pa)
MA	0.075	29.61	4.89	907.31
MB	0.072	24.81	4.51	756.81
MC	0.068	20.21	4.31	501.61

X-ray diffraction of membranes: The X-ray diffractions of the membranes are shown in Fig. 2. From Fig. 2, it's clear that the order of degree of crystallization is MA > MB > MC. It can be explained that the MA has a compact chain

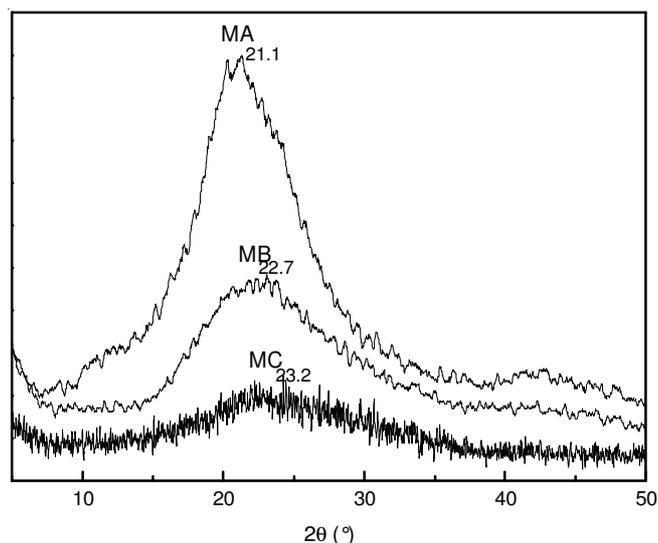


Fig. 2. X-Ray diffraction patterns of membranes

structure and a ship shape form, while the orderliness of the chain structure has been destroyed in MB and MC. Amorphous form were showed in the X-ray diffractions of MB and MC. To MA, a compact chain structure and hydrophobic surface limited ion permeation while MB can convey ions. The results of X-ray diffractions of the membranes are similar to the phenomenon of the solid polymer electrolyte (SPE) of the PEO-salt type. As is generally known, with a solid polymer electrolyte of the polyethylene oxide (PEO)-salt type, decreasing its degree of crystallization can be helpful in improving its ionic conductivity¹⁶. Polyethylene oxide is generally regarded as crown ether of opening chains. Another phenomenon can be observed; the angle of diffraction (2θ) becomes wider from MA to MC indicating that the amorphous areas became bigger.

To sum up, a polymeric membrane (MA) with a higher degree of crystallization tended to show amorphous structure after treated by mixed solutions and electrolysis.

Morphological characteristics of membrane: SEM photographs are shown in Fig. 3. In Fig. 3, MA-1 indicates the surface of the membrane and MA-2 indicates the cross section of the membrane. From the SEM photographs of MA-1 and MA-2, the smooth surface and compact cross section indicate that the polymeric membrane (MA) own a compact structure. The lateral-cut corrugation in the cross section SEM photographs like fibriform is regarded as a characterization of tropism. It is according to the result of the X-ray diffractions of the MA. MB-1 indicates the surface of the membrane after treated by the mixed solutions and MB-2 indicates the cross section. From the SEM of MB, an obvious phenomenon can be seen; some hole appeared in the surface and the cross section of the membrane after treated by the mixed solutions. The holes' diameter are *ca.* 4-5 μm . It is clear that something lost to result the holes. It consists with the phenomenon of the thickness of MA > MB; and on earth the chelation of the polymer containing crown ether group to K^+ is the reasons. It is the reason of structure distinctness between MB and MA in the X-ray diffractions. The loose structure of MB resulted to degree of crystallization descend. MC-1 and MC-2 indicate the surface of the membrane after water electrolysis and MC-3 indicates the cross section of the membrane after water

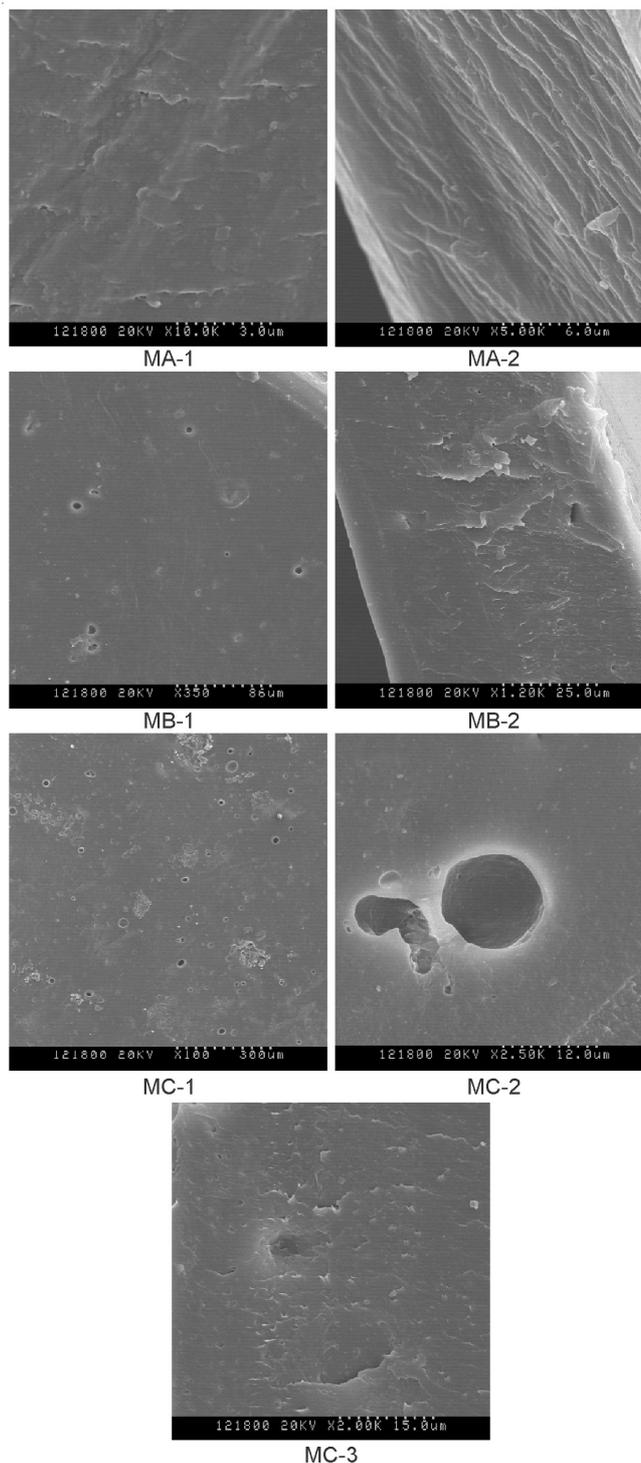


Fig. 3. Scanning electron microscopy of membranes

electrolysis. In the SEM of MC, the holes became bigger through comparing of the MB-1 and MC-1/MC-2. The holes' diameter are *ca.* 8-12 μm . The amount of the holes increased clearly in MC. It consists with the phenomena of the thickness of MA > MB > MC and the crystallization descend in the X-ray diffractions. A reasonable presumption is that the chelation is not complete in MB because the hydrophobic surface led the chelate process lengthy while water electrolysis accelerated the chelate process¹⁷.

Electrochemistry properties of membrane: Raney Ni and the membrane after treated by the mixed solutions (MB)

assembled an electrolytic cell, which is like “sandwich”. The electrochemistry properties of the MB were tested preliminarily.

The relationship between cell voltage/IR drop (between anode and cathode) and time is shown in Fig. 4, testing condition is 25 °C, 5 mol/L KOH, 200 mA/cm². From Fig. 4, cell voltage is 1.845 V and IR drop between anode and cathode is 80 mV. IR drop between anode and cathode consist of IR drop to the MB membrane both sides, IR drop to the solution between anode and cathode (generally ignored) and IR drop to the air bubble from electrolysis. The resistance of the membrane is 0.23 Ω cm², according to the four electrode AC impedance method¹⁸⁻²⁰. Thus, the IR drop to the air bubble from electrolysis can be calculated and it is 34 mV (34 mV = 80 mV – 0.23 Ω cm² × 200 mA/cm²).

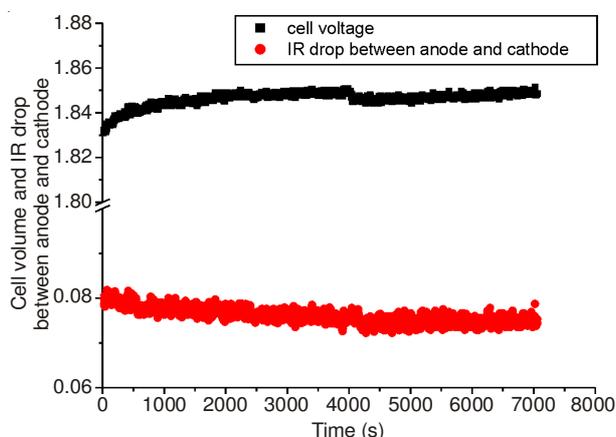


Fig. 4. Relationship between cell voltage/IR drop (between anode and cathode) and time

Fig. 5 showed the relationship between cell voltage and current density in various pH alkaline solutions (testing condition: 25 °C). From Fig. 5, an obvious phenomenon can be seen, the cell voltage dropped gradually with the pH of alkaline solutions increased step by step. While in the same pH of alkaline solutions, the cell voltage ascended gradually with the increase of current density.

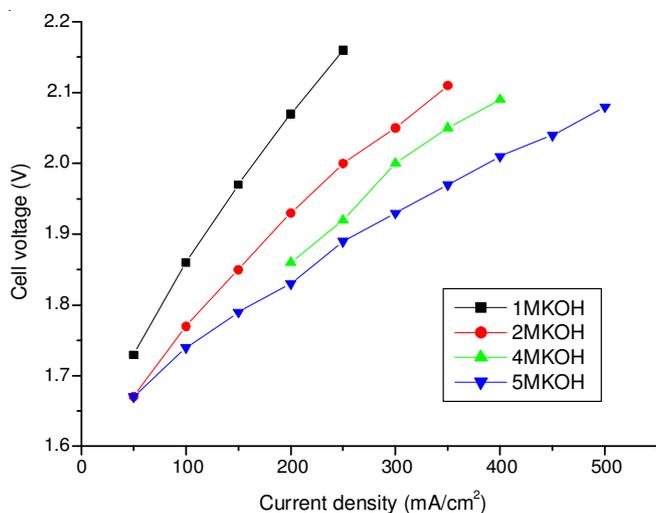


Fig. 5. Relationship of cell voltage and current density in various pH alkaline solutions. (testing condition: 25 °C)

Fig. 6 illustrated the relationship between cell voltage and pH of alkaline solutions. (Testing condition: 40 °C, 200 mA/cm²). From Fig. 6, the cell voltage dropped gradually with the pH of alkaline solutions increased step by step. The cell voltage didn't drop until the density of KOH reached 4 mol/L; maybe it is concerned with the K (the chelation equilibrium constant). From Figs. 5 and 6, the cell voltage dropped with the temperature rose up at the same pH and current density.

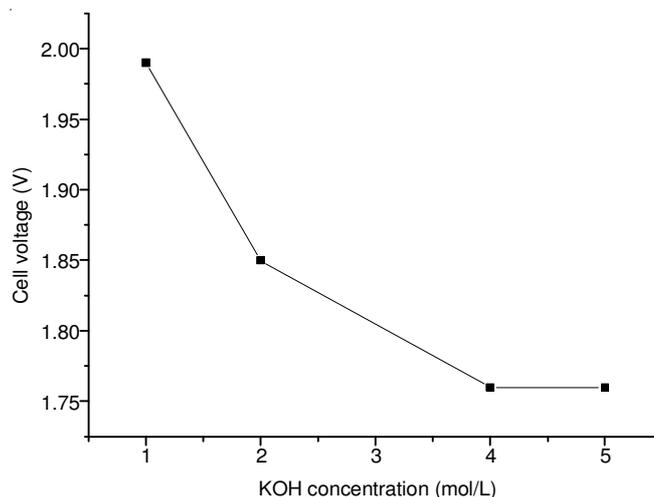
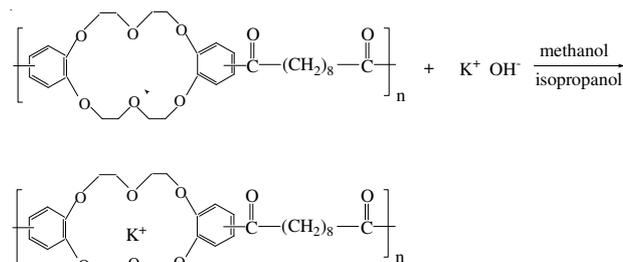


Fig. 6. Relationship between cell voltage and pH of alkaline solutions. (Testing condition: 40 °C, 200 mA/cm²)

Conclusion

In the work, a kind of linear polymer containing crown ether group was synthesized and the membrane was made of the polymer. The membrane was treated by a kind of mixed solution and its form changed from a compact structure to a porous structure. The process is shown as the Fig. 7. The membrane after treated by the mixed solution can be applied to water electrolysis. The electrochemistry properties of the membrane were tested primarily and satisfactory results were obtained. The results are relative to the chelation, so the results are not satisfactory if Na⁺(NaOH) replaced K⁺(KOH) because of different K (chelated equilibrium constant). It has been proved through relative experiment. The resistance of the membrane is 0.23 Ω cm²; the cell voltage is lower than 2.0 V (25 °C, 5 mol/L KOH, 200 mA/cm²). The results encouraged us and further study is needed to test the electrochemistry properties of the membrane in more long time and higher temperature. The durability of the membrane need further study and the next work is proceeding.



OH⁻

Fig. 7. Process of treatment to the membrane

ACKNOWLEDGEMENTS

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