Study of transport through an electro responsive polymer membrane

D Das, A Datta and A Q Contractor

Department of Chemistry, Indian Institute of Technology Bombay Powai
Mumbai-400076 India
E-mail: debasreedas@chem.iitb.ac.in, anindya@chem.iitb.ac.in,
aqcontractor@iitb.ac.in

Abstract. Conducting polymers have been used widely for development of several electronic,
sensing devices because of its electro active nature. In the present work porous polycarbonate
(PC) support was coated with a thin gold layer. An electrochemically synthesized polyaniline
(PANI) film was deposited on gold coated PC and characterisation was done by field emission
gun scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM) and
atomic force microscopy (AFM). For measuring the concentration of potassium ion (K⁺)
inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. Potassium ion
transport across PANI membrane at various potential showed the gradual opening of the coiled
PANI. In this work an effort has been given to picture the situation in the membrane electrolyte
junction on application of potential.

1. Introduction
Conducting polymers are conjugated polymers, which have an extended p-orbital system, having
movement of electrons from one end of the polymer to the other. The most well known are polyaniline
(PANI) and polypyrrole (PPY)) whose unique physical and electronic properties [1, 2] have been
explored in several technologies. Their unusual high conductivities, have helped in the development of
several electronic devices, [3-5] conducting wires, and electrostatic shielding. It is revealed from
literature survey that PANI has a distinct position among the conducting polymers, because of its ease
of synthesis and several applications.

The different forms of PANI in aqueous solutions are reduced, leucoemeraldine and half-oxidized,
emeraldine states. PANI can be reversibly turn on or off in between these states [6]. The transport
properties of these membranes are controllable after synthesis, thereby opening up a new route for
chemical separation [7]. In our work we have synthesized a polymer membrane and looked in to the
transport of potassium chloride across the membrane.

2. Experimental section
Thermal evaporation of gold (200nm) was carried out in HINDHIVAC (model 12A4D) on 1.2 µm
diameter pore size polycarbonate (PC) membrane purchased from Scientific Sales Syndicate in
vacuum evaporation system. GR grades Aniline, potassium chloride (KCl), hydrochloric acid (HCl),
dichloromethane (DCM) were purchased locally. PANI was then deposited on the gold coated
membrane electrochemically from a solution containing 0.1 M aniline in 0.5 M H₂SO₄ (Electronic
grade). The electrode potential was cycled between -0.2 and +0.8 V vs SCE for 40 cycles. Platinum
(Pt) foil was used as counter electrode. The film was then cycled in 0.5M H₂SO₄ to remove the
PANI membranes were characterised by field emission gun scanning electron microscope (FEG-SEM) (JEOL JSM 7600F) and AFM Nanoscope IV. A 6-8 nm layer of Palladium was then sputtered on samples before FEG-SEM imaging. For TEM (JEOL JEM 2100F) DCM was added drop by drop on the membrane containing grid to dissolve the PC leaving behind the polymer on the grid.

### 3. Results and discussion

To observe the transport of K⁺, PANI films of polymerisation charge (28 mC/cm²) were synthesized by potentiodynamic method on the gold coated PC as shown below in figure 2 & 3.

![Figure 2. Cyclic voltammogram of PANI from 0.1 M aniline.](image)

![Figure 3. Cyclic voltammogram of PANI in 0.5 M H₂SO₄.](image)

SEM of PC and PANI deposited on gold coated PC are shown in figure 4, 5. The topographic view depicts that due to deposition of the porous PANI film there is a significant decrease in pore mouth. From TEM in figure 6 it is clearly seen there is a PANI film on the PC but it has not completely blocked the pore mouth. Since the polymer has a tendency to grow more on the hydrophobic walls of the PC, so the growth cannot be inhibited resulting in the formation of tubes. The sectional analysis of AFM in figure 7 revealed that there is around 50% coverage of the pore mouths.

![Figure 4. PC.](image)

![Figure 5. SEM of PANI deposited on PC.](image)

![Figure 6. TEM of PANI tubule.](image)
Due to the electrochemical processes conducting polymers are often accompanied by transport of ions at the interface. The potential across the double layer plays also a role in electrochemical transport through the conducting polymer. The interfacial properties of a PANI membrane can be switched by electrochemical control of the polymer’s oxidation state then the morphology of the polymer undergoes a change on application of electrochemical potential. This change has a huge application in membrane oriented research because the polymer’s different redox states can be controlled by potential. The change in conformation is accompanied by the insertion/expulsion of ions in and out of the polymer chain.

As it can be seen from the above scheme the PC has two sides’ smooth side and rough side. PANI deposited on the gold coated smooth side faces the source solution and the rough side faces the receiver solution. The auxiliary electrode is placed in the source solution due to which there develops an electric gradient between it and the membrane. The time for which the membrane is held at a particular potential is sufficient for a significant amount of transport to take place. Since the auxiliary electrode is kept in the source solution side the transport is mainly ruled by the ion incorporation and expulsion phenomena [8]. The thickness of the PC is around 10µm. The K⁺ ions cross the barrier of the porous PANI membrane, after which it seeps through the walls of the PC to reach the receiver side. The concentration of K⁺ was measured as a function of the polymer oxidation state, which was controlled by stepping the potential applied to PANI film from a lower potential to increasingly higher values from 0.1V to 0.4V. The potential was applied for shorter period of time in order to avoid any
electrochemical degradation of the polymer. The effective area for transport of K$^+$ was 1.45 cm$^2$. In these experiments the driving force is electrochemical stimuli.

Table 1. Flux of K$^+$ through PANI at different potentials

| Potential(V) | Flux of K$^+$ (10$^{-8}$ mol/cm$^2$/s) |
|--------------|--------------------------------------|
| 0.1          | 0.87                                 |
| 0.2          | 1.098                                |
| 0.3          | 1.336                                |
| 0.4          | 1.406                                |

Studies with K$^+$ were mostly done with atomic absorption spectrometry by the group of Wallace. In our case the concentration of K$^+$ was measured by (ICP-AES) which improves in precisely the quantification. When a potential is applied due to oxidation of the polymer incorporation of anions and release of cations take place. The extent of transport depends on the relative mobility of the cations and anions. Hence for electrochemical transport the movement of the ions play a significant role [9]. Due to this uptake of anions there occurs volume swelling which results in increase in flux through the polymer. The transport is found to depend on the morphology of the polymer. On going from 0.1V to 0.4V the flux is found to be reasonably high near the 0.4V as shown in figure 8 and table 1 because here PANI exists in half oxidised state which as shown in figure 2 corresponds to the highest conductive state of PANI. The increase in flux of K$^+$ with application of positive potential through PANI membrane with gradual increase of potential shows the opening of the coiled PANI to more expanded and porous structure.

4. Conclusion

SEM, AFM, TEM images show that layer of PANI has been successfully deposited without plugging the pore mouths. The transport of K$^+$ through porous PANI demonstrated the interfacial responses in the membrane electrolyte interface with the application of electrochemical stimuli. The transport process showed how the polymer undergoes change in conformation from coiled to more expanded and porous structure with the application of potential signifying the electro active nature of PANI.

5. References

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