Redox Reactions without Direct Contact of the Reactants. Electron and Ion Coupled Transport through Polyaniline Membrane

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It is demonstrated that Fe^{3+} in one solution can be reduced to Fe^{2+} by ascorbic acid in another solution when both aqueous solutions are separated by polyaniline membrane. This transmembrane redox process is possible due to electron/anion coupled counter transport through polyaniline membrane. It was demonstrated that at least one of the solutions must have acidic pH to initiate the transmembrane redox reaction. Both redox processes on the solution/membrane interfaces and the electron/ion coupled transport through the membrane play important role in determining the rate of transmembrane reaction. Possible kinetic mechanism is proposed. Apparent "diffusion coefficients" for redox equivalents inside polyaniline membrane and the rate constants of redox reactions on both solution/membrane interfaces are estimated. Maximal transmembrane reaction rate is 2×10^{-9} mol/(s cm^2) in terms of transport of redox equivalents through the membrane and formation of Fe^{2+}. This value is much higher than the typical values of the rates of respiration in mitochondria expressed in the same units. For thin membranes, the rates of transmembrane redox reactions are determined by interface processes and characteristic times are comparable to those in biomembranes.

1. Introduction

Transmembrane redox processes are extremely important in biological systems, and the most well-known examples are cellular respiration and photosynthesis. It was possible to imitate some physicochemical aspects of these processes using polymer supported liquid membranes with quinones serving as mobile carriers in a coupled electron and proton co-transport in the same direction across the membrane.[1,2] In some other cases, for example in liquid membranes with mobile derivatives of ferrocene, electron transport is coupled with counter transport of anions through the membrane into opposite direction.[3−5]

Another possible option to conduct transmembrane redox reactions could be based on electroconductive polymer membranes, for example polyaniline. Redox properties of polyaniline (PANI) have been intensively investigated and characterized by XPS, cyclic voltammetry, and impedance.[6−9] It was found that PANI coating on the surface of electrodes incorporates and releases anions as the result of the redox reactions.[10] This could find potential applications in sensors for biologically important analytes and in other bioelectronic devices, where biological components can be closely integrated with electronic systems.[11,12]

PANI membranes in the undoped and HCl doped states have not only different electrical conductivity determined by electron mobility, but also completely different H^+ permeability and ion selectivity.[13] Direct measurements of the H^+ transport through the PANI membrane separating two aqueous solutions confirm that the H^+ ion is able to penetrate through the membrane together with Cl^-.[14]

PANI films are able to reduce $FeCl_3$ in the presence of HCl.[15] The reaction kinetics is characterized by two phases and is highly dependent on preliminary doping of the PANI films. The initial fast kinetic phase is determined by reduction of Fe^{3+} on the surface, whereas the second one is slower and is dependent on transport of electrons from the bulk volume of the polymer film to the surface and Cl^- anions in the opposite direction. These unique properties are possible because of the simultaneous and relatively high permeability of both electrons and ions in polymers called synthetic metals, such as doped polyaniline,[16] and usually are not observed in common metals, having only electron conductivity.

The purpose of this paper is to demonstrate that it is possible to conduct transmembrane redox reactions using solid polymer membranes based on polyaniline. This material is permeable to both electrons and ions, which results in an electroneutral process of coupled electron and ion transport through the membrane. In this work, the simple redox reaction $FeCl_3$ + HCl/ascorbic acid was chosen to demonstrate this process. It was shown that the transmembrane transport of electrons (redox equivalents) from one solution into another and coupled Cl^- transport in the opposite direction are possible and depend on the properties of aqueous/membrane surfaces and the polymer matrix itself. Kinetic parameters of these steps were determined. The rate of this transmembrane reaction through the solid membrane was comparable or even higher than that of the transmembrane redox reactions through liquid supported membranes.[1,2]

It is important that, as a result of these reactions, one is able to produce new substances without direct contact and mixing of initial reactants, which means that the separation and purification of the final products could be much easier. In this case, we can see some parallels with biological phenomena both from the functional point of view and mechanism. For example, it is well-known that transmembrane redox reactions coupled with ion transport are possible in plant leaf chloroplasts, liver mitochondria, and microsomes. These types of reactions are possible due to the presence of not only mobile carriers like coenzyme Q but mainly due to the channel forming proteins where ions and electrons are moving through the membrane.

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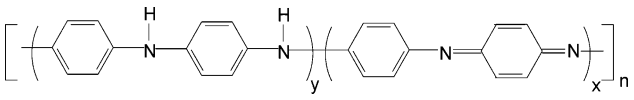
2. Experimental Section

The PANI synthesis and PANI film casting method has been described before.[13] The films were made by evaporation of *N*-methyl-2-pyrrolidinone (NMP) solutions of PANI**,** and were in the emeraldine base form (EB), which means the intrinsic oxidation state has $x = 0.5$ in the general formula:



The membrane had thickness of 20∼250 μm, depending on the amount of PANI used.

The membrane chamber and other details of the experiments were also described previously.[14] The volume of each cylindrical Teflon semichamber, separated from the other one by PANI film, was 50 mL. The membrane contact area was 4.9 cm^2. At the very beginning of the redox experiment, one side of the membrane chamber was filled with an oxidant ($FeCl_3$ solution at proper pH and concentration) and the opposite semi-chamber was empty. The membrane was preequilibrated by stirring this oxidant solution for more than 10 h until the redox potential in this solution measured with Pt electrode versus Ag/AgCl reference electrode became relatively stable. The membrane before and after reaction with Fe^{3+} was earlier characterized with XPS.[13] In the presence of HCl, the membrane becomes doped and electroconductive, which was demonstrated using impedance measurements, and its DC resistance decreased from several megaohms by six orders of magnitude. After the preequilibration, the reducing agent (ascorbic acid solution) was added into the opposite semichamber. Both solutions were stirred with mechanical stirrers.

Detailed methods of redox potential measurement and [Fe^{2+}] calculations are described elsewhere.[15] The influence of the $FeCl_3/FeCl_2$ ratio, pH, and anion concentration on the redox potential of the $FeCl_3/FeCl_2$ + HCl system was calibrated systematically with the standard additions method.[15]

The transmembrane potential was measured with two Ag/AgCl electrodes with KCl-agar salt bridges. Its value and also redox potentials and pH in both solutions were registered continuously. The transmembrane potential and the difference of redox potentials in the two solutions were practically equal.

Ascorbic acid (Aldrich) was used without further purification. 0.001 M EDTA was added into this solution to eliminate the possible catalytic effect of the metal ions from impurities. The pH changes in ascorbic acid solution as a function of the HCl addition were preliminarily determined. Oxidation of ascorbic acid simultaneously results in H^+ formation, shown by the following equation, where A represents dehydroascorbic acid:

$$H_2A \rightarrow 2H^+ + A + 2e^- \qquad (1)$$

The half-cell reaction $Fe^{3+} + e^- \rightarrow Fe^{2+}$ can be combined with the eq 1, to give the whole-cell reaction $2Fe^{3+} + H_2A = 2Fe^{2+} + 2H^+ + A$.

The H^+ transport rate through PANI membrane to the side containing ascorbic acid was calculated as the rate of [H^+] change in ascorbic acid solution minus the electron transport rate, equal to the rate of Fe^{2+} formation in the oxidant solution.

3. Results

3.1. Transmembrane Redox Reaction and H^+ Transport. Initially a few redox couples were used to examine the possibility of transmembrane redox reactions through PANI films, such as $FeCl_3$ + HCl/$FeCl_2$ + HCl, $FeCl_3$ + HCl/ascorbic acid, $K_3Fe(CN)_6$/ascorbic acid, etc. In a typical experiment, the oxidant was 0.01 M $FeCl_3$ + 0.3 M HCl, and the reducing agent was 0.05 M ascorbic acid + 0.001 M EDTA. The initial pH of the reducing solution was around 2.7. Direct diffusion rates of ascorbic acid, Fe^{3+} and Fe^{2+} through the PANI membrane were less than 10^{-12} mol/(s cm^2), and were determined by measuring the concentrations of Fe^{3+} and Fe^{2+} colorimetrically with NaCNS and 2,4,6-tri-2-pyridyl-s-triazine, respectively. After the equilibrium between the oxidant and the membrane was practically achieved, ascorbic acid was added into the opposite chamber, causing the observed immediate decrease of the reduction potential in the oxidant. The formation of [Fe^{2+}] in the oxidant solution and the electron transfer across the membrane was also independently verified by characteristic color changes after the addition of 2,2′-dipyridyl into this solution. No evident time lag was detected.

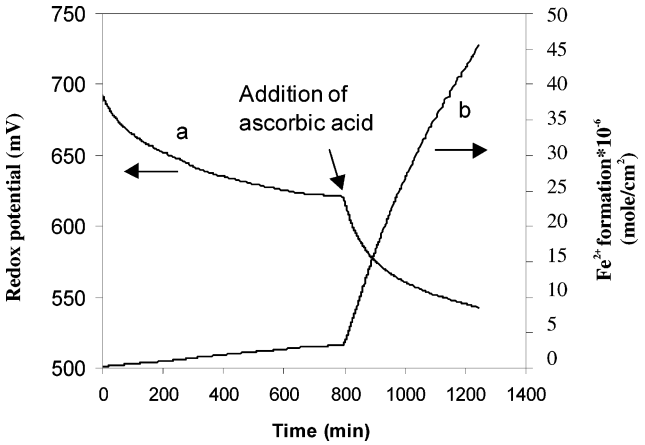


Figure 1. Typical redox potential and calculated amount of Fe^{2+} formed in $FeCl_3$ solution as a function of time. Oxidant: 0.01M $FeCl_3$+0.3M HCl; Reducing agent: 0.05 M ascorbic acid, pH = 2.8.

When the pH in both reducing and oxidant solutions was larger than 3.0 and the film was undoped, the transmembrane redox reaction rate was less than 10^{-12} mol/(s cm^2). The addition of H^+ in one of the solutions greatly increased the transmembrane reaction rate. It was found that ascorbic acid was the most effective among a few different reducing agents, such as $Na_2S_2O_3$, KI, etc. This may be due to the fact that ascorbic acid is an acid itself and can interact with PANI molecules more easily. The N1s core-level XPS spectra of the 0.05 M ascorbic acid treated PANI film demonstrated that the relative contents of imine (═N─), amine (─N─) and positively charged nitrogen atoms are near 26%, 63%, and 10% respectively, corresponding to the partially doped PANI.

We were able to reduce near 50% of $FeCl_3$ 6 h after the addition of ascorbic acid (Figure 1). The initial reaction rate was about 2×10^{-9} mol/(s cm^2) in terms of the formation of $FeCl_2$, which is much larger than the estimated direct iron ion transport rate. The redox potential in the reducing solution went up, corresponding to the oxidation of ascorbic acid.[17] However, due to the instability of H_2A in the open air and the sluggish response of redox potential measurements, instead of directly measuring the oxidation of H_2A to A, we calculated the transmembrane reaction rate only based on the redox potential measurements in $FeCl_3$ solution.

The role of H^+ doping in the direct reaction between PANI and Fe^{3+} has been demonstrated previously.[15] Figure 2 shows the transmembrane reaction rate as a function of [HCl] in the oxidant solution. The rate increased with H^+ concentration, then reached a maximum value and finally slowly decreased as the

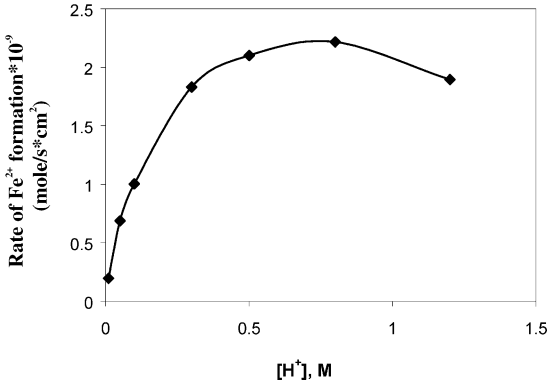


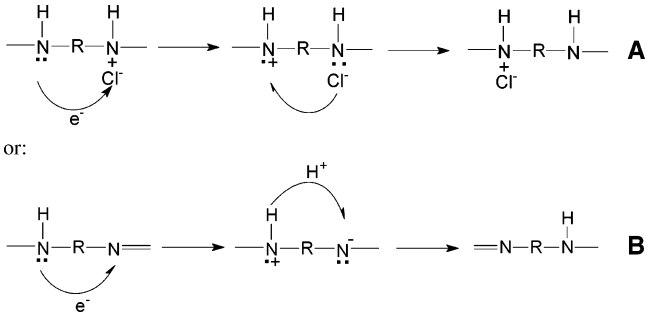
Figure 2. Influence of H^+ in the oxidant phase on the rate of transmembrane redox reaction. Oxidant: 0.01 M $FeCl_3$ + HCl; reducing agent: 0.05 M ascorbic acid, pH = 2.7.

$[H^+]$ in oxidant solution increased further. Probably HCl can increase both the reaction rate on the PANI/oxidant interface and the electron/Cl^- coupled transport inside the PANI membrane (see Scheme 2). The Cl^- transmembrane transport is possible because if the membrane is doped it has higher permeability of Cl^- than that of H^+.[13] On the other hand, the formation of complexes $[FeCl_x]^{3-x}$ at HCl concentration more than 0.8M resulted in the decrease of transmembrane reaction rate.

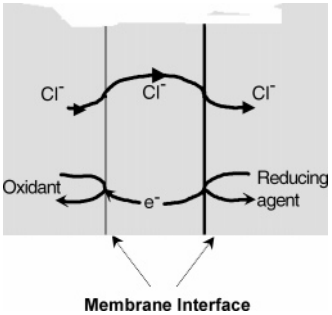
Increase of the initial ascorbic acid concentration also resulted in the increase of reaction rate, but the rate reached a plateau when the concentration was above 0.25 M (Figure 3). The process was accompanied by pH decrease in the ascorbic acid solution (Figure 4). The steady-state rate of this process was much higher because it was determined by both transmembrane chemical reaction and direct H^+ transport due to the concentration difference across the membrane.

Influence of the $FeCl_3$ concentration on the transmembrane reaction and H^+ transport rate is presented in Figures 5 and 6,

SCHEME 1: Possible Schemes of the Electron Transfer from Amine Nitrogen to Its Neighboring Nitrogen



SCHEME 2: Scheme for Facilitated Electron/Cl− Counter Transport through the PANI Membrane in the Presence of Oxidant and Reducing Agent at Different Sides of the Membrane



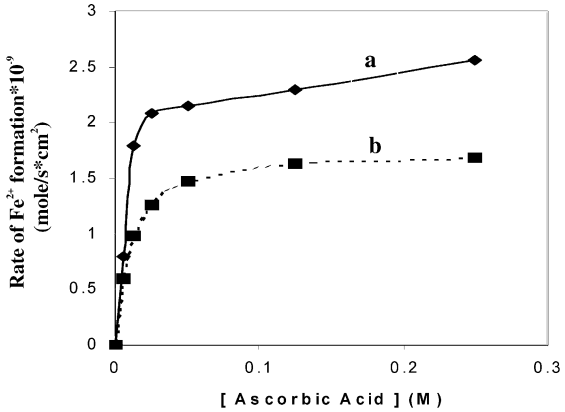


Figure 3. Influence of the concentration of ascorbic acid on the rate of transmembrane redox reaction. Oxidant: 0.01 M $FeCl_3$ + 1 M HCl. Membrane thickness: ~120 μm; a: experimental results; b: simulated results based on eq 13.

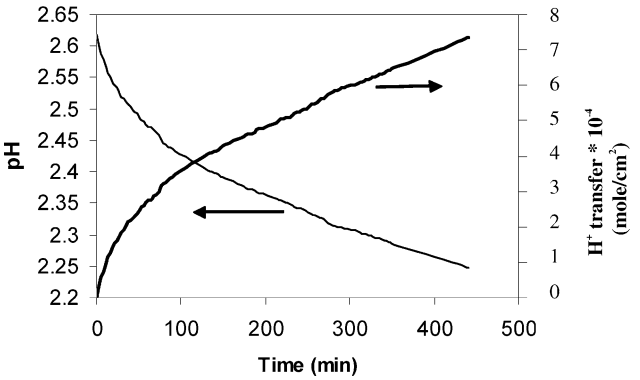


Figure 4. Typical pH changes and calculated H^+ addition in the ascorbic acid solution. Oxidant: 0.01 M $FeCl_3$ + 0.3 M HCl; reducing agent: 0.05 M ascorbic acid.

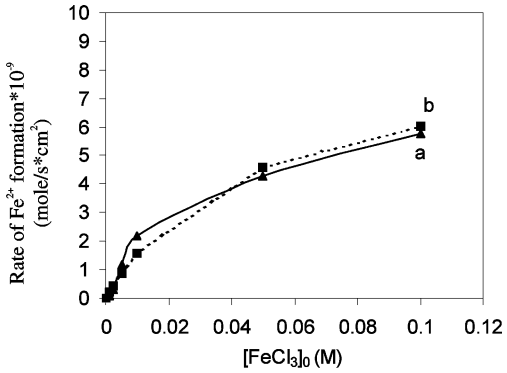


Figure 5. Influence of the initial concentration of $FeCl_3$ on the rate of transmembrane redox reaction in the presence of 1 M HCl. Reducing agent: 0.05 M ascorbic acid, $pH_0 \sim 2.7$. Membrane thickness: ~20 μm. a: experimental results; b: simulated results based on the eq 13.

respectively. It can be seen that the H^+ transport rate increased by about 15 times when $[Fe^{3+}]$ increased from zero to 0.1 M (see Figure 6), and its value is about three times higher than that of the transmembrane redox reaction rate. This result again demonstrates that the H^+ transport is not strictly coupled with electron transport. Earlier we demonstrated that the greater the intrinsic oxidation state of the PANI membrane, the greater the permeability for H^+ and coupled anions.[15] Addition of $FeCl_3$ increases the intrinsic oxidation state of PANI film, and as a result, the H^+ transport rate is increased.

Figure 7 shows the comparison of H^+ transport rates with and without redox processes as a function of [HCl] in the more acidic solution. The H^+ transport exhibits similar dependence

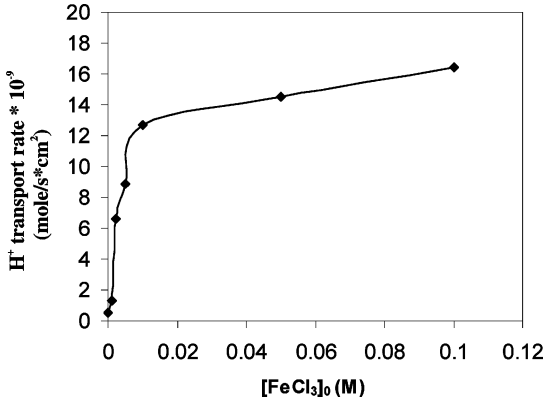


Figure 6. H^+ transport rate as a function of the initial concentration of $FeCl_3$ in the presence of 1 M HCl. Reducing agent: 0.05 M ascorbic acid, $pH_0 \sim 2.7$.

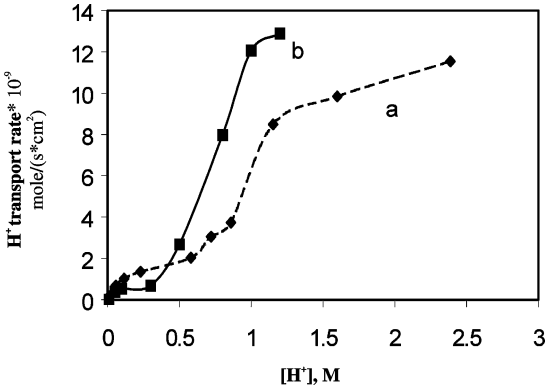


Figure 7. Influence of H^+ in acidic solution on H^+ transport with and without redox processes a: HCl/buffer, pH 6.47 (without redox process); b: 0.01 M $FeCl_3$ + HCl/0.05 M ascorbic acid, pH 2.7 (with redox process).

on [HCl] in these two cases, which is evidently higher at high $[H^+]$ in the presence of redox process as compared to the direct H^+ transport without redox process.

3.2. Influence of Anions on the Transmembrane Reaction and H^+ Transport. To demonstrate the role of anions in the coupled electron and ion transport, 0.2 M camphor sulfonic acid (CSA) was used instead of HCl. No evident changes were detected in the redox potential and pH value of both oxidant and reducing agent solutions even after 4 days. Evidently, counter transport of anions is coupled with electron transport. Since CSA has a very big anion, it cannot penetrate through the PANI membrane. As a result, transmembrane electron transport also stops.

The influence of KCl in the oxidant solution on transmembrane redox rate and H^+ transport rate is presented in Figure 8. It was found that the Cl^- anion in the oxidant solution has no significant influence on the reaction rate (Figure 8a). In contrast, it evidently increased the H^+ transport (Figure 8b), implying that the H^+ transport is mainly driven by the ion concentration gradient rather than the redox potential difference.

Figure 9 shows the influences of KCl concentration in the reducing solution on the transmembrane reaction (a) and H^+ transport rate (b), respectively. Both transmembrane reaction and H^+ transport rates showed evident decrease due to increase of Cl^- concentration in this case.

3.3. Influence of Membrane Thickness on the Transmembrane Reaction Rate and H^+ Transport. Figure 10 shows the inverse transmembrane reaction rate as a function of membrane thickness. At high H^+ concentration, the membrane

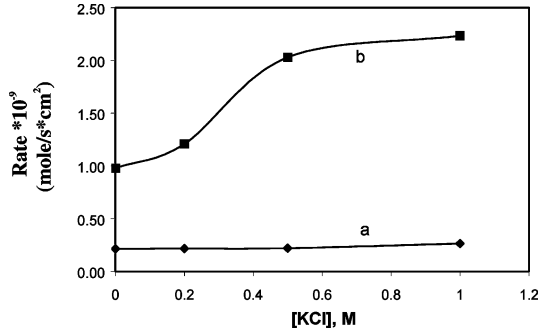


Figure 8. Influence of KCl in $FeCl_3$ solution on the redox rate (a) and H^+ transport rate (b). Oxidant: 0.01 M $FeCl_3$ + 0.1 M HCl + KCl, Reducing agent: 0.05 M ascorbic acid, pH 2.7. Membrane thickness 230 μm.

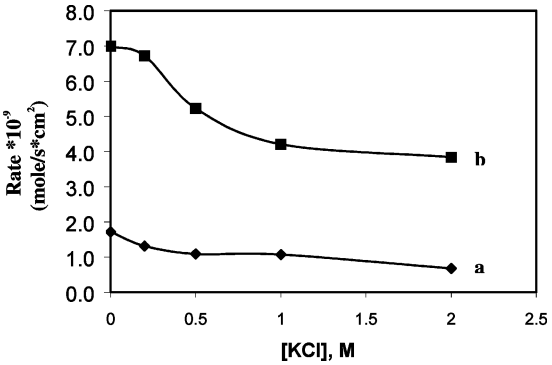


Figure 9. Influence of KCl in ascorbic acid solution on the redox rate (a) and H^+ transport (b). Membrane thickness 230 μm. Oxidant: 0.01 M $FeCl_3$ + 1 M HCl; Reducing agent: 0.05 M ascorbic acid + KCl.

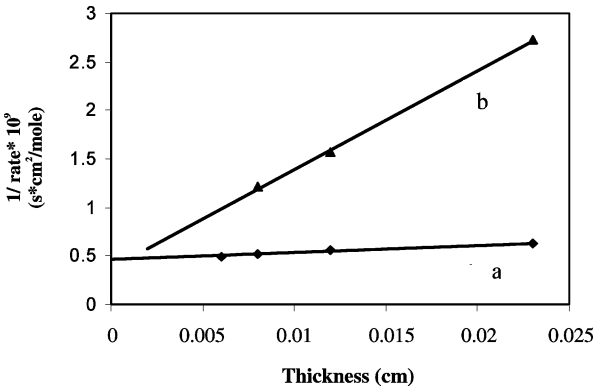


Figure 10. Inverse transmembrane redox reaction rate as a function of membrane thickness. Oxidant: 0.01 M $FeCl_3$ + HCl; Reducing agent: 0.05 M ascorbic acid; a: [HCl] = 1 M; b: [HCl] = 0.1 M.

thickness almost did not influence the process (Figure 10a). In this case, the PANI molecules were fully doped, the resistance for electron and ion coupled transport in the PANI membrane was low, and the transmembrane reaction rate was determined by the reactions on the interfaces.

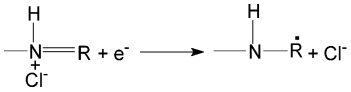
At lower H^+ concentration (0.1 M), the electron-transfer resistance of the PANI membrane was higher than that of the interfaces (Figure 10b), and the membrane thickness plays an important role in determining the transmembrane reaction rate. The absolute value of the interphase resistance determined as the intercept with *Y* axis was almost the same in both cases.

4. Discussion

Experimental results demonstrated that ascorbic acid and Fe^{3+} separated by the PANI membrane could be oxidized/reduced,

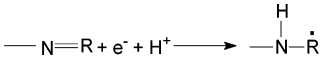
respectively, without direct contact with each other. The solid polymer membrane here acted as electron and ion permeable medium necessary for this chemically driven electron and ion coupled transport.

The membrane based redox process consists of three steps in series, i.e., reactions on the two membrane/solution interfaces and one coupled charge counter transport step inside the PANI membrane. At the interface between the reducing agent and the PANI membrane, the electrons are transported from the reducing agent into the PANI film, coupled with anion movement through the interface in the opposite direction to keep the electro neutrality both in the solution and the PANI film. As a result, ascorbic acid was oxidized and the protonated and the unprotonated imine nitrogens in the PANI membrane were reduced into amine according to following reactions:



(2)

or:



(3)

The first reaction (eq 2) probably plays a dominating role in determining the rate at this interface. This mechanism is supported by the fact that the addition of KCl in the reducing agent retards the transmembrane reaction (Figure 9).

In this case, the rate of interfacial electron transfer can be simply expressed by the following equation:

$$F_R = k_R[\{Im\}]_R[H_2A] = k_R(C - [Am]_R)[H_2A] \quad (4)$$

$[Im]_R$: specific content of imine nitrogens in the PANI membrane near the surface, facing reducing solution, mol/cm^3;

$[Am]_R$: specific content of amine nitrogen near the surface of the PANI membrane, facing reducing solution, mol/cm^3;

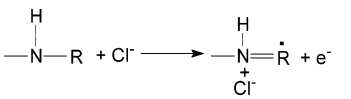
C: total content of amine and imine groups near the surface of the PANI membrane, facing reducing solution; $C = [Im]_R + [Am]_R$, mol/cm^3;

F_R: redox flux through the surface of the PANI membrane, facing reducing agent solution, mol/(s cm^2);

k_R: the rate constant of imine nitrogen reduction, cm^4/(s mol).

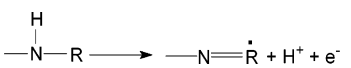
The concentrations here are not given in the unit of mol/cm^2, as is common for example in the heterogeneous catalysis but in mol/cm^3. This is possible because the redox reactions in the case of polyaniline are taking place not only on the surface but also inside the polymer, where electroneutrality is possible because of the simultaneous transport of electrons (redox equivalents) and ions in the synthetic metal materials.[15]

At the opposite membrane interface, electrons are released from the PANI film to the oxidant in the solution. This process is also coupled with ion transport through the solution/PANI membrane interface. As a result, Fe^{3+} is reduced into Fe^{2+}. Amine nitrogen is oxidized and forms protonated or unprotonated imine radical depending on the local oxidation state and pH:



(5)

or:



(6)

At low HCl concentrations, the dominating process is described by eq 6. At high HCl concentration the membrane is more permeable to anions; therefore probably anion insertion is the dominating process (eq 5).[13]

Electron transfer for the oxidant/PANI membrane interface can be expressed as

$$F_o = k_o[Am]_o[Fe^{3+}] \quad (7)$$

$[Am]_o$: specific content of amine nitrogen in the membrane near the surface facing oxidant solution, mol/cm^3;

k_o: rate constant of amine nitrogen oxidation, cm^4/(s mol);

F_o: electron flux at the oxidant/membrane interface, mol/(s cm^2), equal to the rate of Fe^{3+} reduction.

Two different transport phenomena are dominating inside the PANI membrane. One is the proton and anion coupled transport purely due to the acid concentration gradient across the membrane. The other one is the coupled electron and ion transport due to the intrinsic oxidation state gradient along PANI molecule chains. These two types of transport are somehow correlated since the intrinsic oxidation state influences the ion permeability.[15] Two possible mechanisms of the electron transfer from amine nitrogen to its neighboring imine nitrogen are shown in Scheme 1. For simplicity, we just consider the ion/electron coupled transport caused by the intrinsic oxidation state gradient along the PANI molecule chain.

In reaction A (Scheme 1), the electron first jumps from amine nitrogen to its neighboring imine nitrogen, followed by the anion transport in the opposite direction. In reaction B, the electron transport is coupled with the H^+ transport in the same direction.

Reaction A is probably the dominating mechanism when the PANI membrane is doped. That is why addition of KCl to ascorbic acid decreased the transmembrane reaction rate. Earlier we have also demonstrated the PANI membrane becomes anion-selective in the doped state.[13]

For simplicity, we assume that the electron/ion coupled transport inside the membrane is proportional to the gradient of the intrinsic oxidation state, i.e., the gradient of specific content of amine nitrogen. Based on this assumption, we have

$$F_T = \frac{D}{L}([AM]_R - [AM]_o) \quad (8)$$

F_T: electron flux across PANI membrane, mol/(s cm^2);

D: effective diffusivity of redox equivalent in the PANI membrane, cm^2/s. For simplicity, we assume that D is position independent;

L: membrane thickness, cm.

At the steady state, $F_R = F_O = F_T$. Solving eqs 4, 7, and 8 together, we finally get

$$F = \frac{1}{\frac{L}{DC} + \frac{1}{k_R[H_2A]C} + \frac{1}{k_o[Fe^{3+}]C}} \quad (9)$$

In the case of low $[H_2A]$ and excess concentrations of HCl and Fe^{3+}, the flux is independent of the membrane thickness and Fe^{3+} concentration, and eq 9 can be simplified

$$F = k_R C[H_2A] \quad (10)$$

Based on the slope of the initial linear part of Figure 3, we have $k_R C = 1.6 \times 10^{-4}$ cm/s.

In the case of low $[Fe^{3+}]$ and excess of HCl and H_2A, we have

$$F = k_o C[Fe^{3+}] \quad (11)$$

and based on the slope of the initial linear part of Figure 5a, $k_oC = 1.9 \times 10^{-4}$ cm/s.

Assuming that C is near 10^{-2} mol/cm^3, we have that the interfacial reaction rate constants are approximately 2×10^{-2} cm^4/(s mol).

When [Fe^{3+}] and [H_2A] are fixed and the membrane thickness is variable, the equation for the flux can be transformed into

$$\frac{1}{F} = \frac{L}{DC} + \text{const} \quad (12)$$

This equation shows that $1/F$ is a linear function of the membrane thickness, which corresponds to Figure 10. At different HCl concentrations, the slope of the line is different, which means that D is a function of [HCl]. When [HCl] is equal to 1 M in oxidant solution, DC is 1.4×10^{-11} mol/(s cm). Corresponding value of D is 1.4×10^{-8} cm^2/s. The diffusion coefficient for HCl diffusion in the system 1 M HCl/PANI/H_2O calculated based on permeability data was 4×10^{-8} cm^2/s[18] and 2.4×10^{-8} cm^2/s.[14] The similarity demonstrates that diffusion of the chloride anion is the rate-limiting step in both cases. At [HCl] equal to 0.1 M, DC determined from the redox transport measurements is equal to 1.0×10^{-11} mol/(s cm) and D is 1×10^{-9}cm^2/s.

It is known that the doped polyaniline films have near 15% of water.[13] Assuming that the water forms thin layers between fibrils,[13] serving as channels for chloride transport, we have the diffusion coefficient through the thin layers of water, equal to 1×10^{-7} cm^2/s. This number is less than the diffusion coefficient in the bulk water ($\sim 10^{-5}$ cm^2/s) and is determined by hopping of chloride ions in the thin and structurized layers of water from one to another amine group of PANI.

On the basis of the previous derivation and standard fitting of Figures 3, 5, and 10, we finally have the expression for the transmembrane reaction rate as a function of [H_2A] and [Fe^{3+}] in the presence of 1 M HCl in oxidant solution

$$F = \frac{1}{7.1 \times 10^9 L + \dfrac{1}{1.6 \times 10^{-4}[H_2A]} + \dfrac{1}{1.9 \times 10^{-4}[Fe^{3+}]}} \quad (13)$$

On the basis of the eq 13, we can calculate the transmembrane reaction rate at different conditions. The results are shown in Figures 3 (curve b) and 5 (curve b), respectively. Satisfactory agreement is reached between the experimental and calculated results. If the concentrations of ascorbic acid and Fe^{3+} are high enough, the rate of transmembrane reaction reaches a maximum, and for the membrane thickness 10^{-2} cm, the value is 1.4×10^{-8} mol/(s cm^2). Multiplying this value by the Faraday number, we have the equivalent value of the transmembrane electrical current near 1.4 mA/cm^2, which is common for electrochemical experiments with polyaniline based electrodes.[19]

If the membrane were thin, the transmembrane redox rates would be determined by the interface chemical processes. Even if we assume that the concentrations are far from saturation, and are for example near 10^{-6} mol/cm^3, we would still have the rates on the order 10^{-10} mol/(s cm^2).

It is interesting to compare this rate with the rates of transmembrane redox processes in biological systems. For example, respiration rates in rat liver mitochondria are in the range of $0.1 \sim 2 \times 10^{-9}$ mol of oxygen/s per mg of protein.[20] The corresponding membrane area of the mitochondria is near $1 \sim 5 \times 10^3$ cm^2, which gives the respiration rates in the range 2×10^{-14} to 2×10^{-12} mol/(s cm^2). This value is several orders of magnitude less than the maximal rates in the case of PANI membranes, assuming that chemical steps are fast in the last case.

Another interesting way to compare the processes would be to analyze characteristic times or turnover numbers which are dependent on concentrations of substrates. Characteristic times for diffusion through a membrane can be estimated based on well-known Einstein-Barrer equation

$$\tau = \frac{L^2}{6D}$$

For biological membranes having a thickness near 5×10^{-7} cm and $D = 10^{-7}$ cm^2/s, we have a characteristic time of 0.4 μs. The antibiotic valinomicyn in biological membranes has the characteristic time for transmembrane translocation near 50 μs.[21]

For the interface processes, we can assume that the interface redox reaction is localized in a thin layer, say near 10^{-7} cm. The product kC (cm/s) has a simple physicochemical meaning and is similar to mass transfer coefficients in mass transport. Dividing this product by thickness, we have an estimate of the turnover number for the interface redox reaction, which is near 1.5×10^3 s^{-1}. In comparison, the most active pure cytochrome bc(1) complex participating in the intermolecular electron transfer has a turnover number of 800 s^{-1}.[22]

5. Conclusions

The reduction of Fe^{3+} to Fe^{2+} by ascorbic acid, separated by a PANI membrane, and chemically driven electron/ion coupled transport through a PANI membrane were demonstrated. Factors influencing the coupled transport were systematically investigated. It was demonstrated that at least one of the solutions must have an acidic pH to have the membrane doped and to initiate the transmembrane redox reaction. Chloride anions are the ions transported in the opposite direction to the electron transport. A possible electron/ion coupled transport mechanism was proposed. A kinetic model simulating the experimental results was suggested. The apparent diffusion coefficient of redox equivalents in the PANI membrane is determined by chloride mobility, and for the membrane in contact with 1 M HCl, the corresponding value is $D = 1.4 \times 10^{-8}$ cm^2/s. The rate constants on the solution/membrane interface were estimated, and the values of k both for reactions of PANI with ascorbic acid and ferric chloride were near 2×10^{-2} cm^4/(mol s). Based on this analysis, it was demonstrated that, if the membrane were much thinner, the rate of transmembrane reaction would be limited by the interface processes and their characteristic times are comparable to the parameters observed in mitochondria membranes.

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References and Notes

(1) Kocherginsky, N. M.; Goldfeld, M. G.; Osak, I. S. *J. Membr. Sci.* **1989**, *45*, 85.
(2) Kocherginsky, N. M.; Goldfeld, M. G.; Osak, I. S. *J. Membr. Sci.* **1991**, *59*, 1.
(3) Igawa, M.; Takabayashi, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1561.
(4) Matsumura, M.; Ohno, T.; Saito, S.; Ochi, M. *Chem. Mater.* **1996**, *8*, 70.
(5) Kocherginsky, N. M.; Grishchenko, A.; Tan, D. In *NAMS, 11 Annual Conference*; Pelegrino, J., Rasco, T., Yetzbacher, M., Eds.; NIST: Boulder, CO, 2000; p 249.

(6) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci*. **1998**, *23*, 277.
(7) Cassidy, J. F. In *Electroactive Polymer Electrochemistry, Part 2: Application*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1996; p 88.
(8) Deslouis, C.; Musiani, M. M.; Tribolet, B. *J. Phys. Chem.* **1996**, *100*, 8994.
(9) Hatchett, D. W.; Josowicz, M.; Janata, J. *J. Phys. Chem.* **1999**, *103*, 10992.
(10) Trivedi, D. C., In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2, p 505.
(11) Bartlett, P. N.; Cooper, J. In *Electroactive Polymer Electrochemistry, Part 2: Application*; Lyons, M. E. G., Ed.; Plenum Press: New York, 1996; p 233.
(12) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19.
(13) Lei, W.; Kocherginsky, N. M. *Synth. Met*. **1999**, *106*, 19.
(14) Lei, W.; Kocherginsky, N. M. *J. Membr. Sci*. **2000**, *167*, 135.
(15) Lei, W.; Kocherginsky, N. M. *React. Funct. Polym*. **2000**, *45*, 65.
(16) Geni_, E. M.; Tsintavis, C. *J. Electroanal. Chem.* **1985**, *195*, 109.
(17) Kocherginsky, N. M.; Swartz, H. M. *Nitroxide Spin Labels*; CRC Press: Boca Raton, FL, 1995; pp 68−73.
(18) Deslouis, C.; Musiani, M. M.; Tribollet, B. *J. Phys. Chem.* **1994**, *98*, 2936.
(19) Huang, W. S.; Macdiamid, A. G.; Epstein, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, *10*, 1784.
(20) Lionetti, L.; Iossa, S.; Brand, M. D.; Liverini, G. *Mol. Cell. Biochem.* **1996**, *158*, 133.
(21) Tien, H. T.; Ottova-Leitmannova, A. *Membrane Biophysics as viewed from experimental bilayer lipid membranes*; Elsevier: Amsterdam, 2000; p 273.
(22) Yu, C. A.; Wen, X. L.; Xiao, K. H.; Xia, D.; Yu, L. *Biochim. Biophys. Acta* **2002**, *1555*, 65.