Study of sulfur dioxide crossover in proton exchange membrane fuel cells

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\textbf{A B S T R A C T}

As one of the most deleterious impurities to proton exchange membrane fuel cells (PEMFCs), sulfur dioxide (SO\textsubscript{2}) in air can pass through the membrane from the cathode to the anode and poison the catalyst of the two electrodes. The phenomenon of SO\textsubscript{2} crossover is investigated electrochemically in this paper. The influences of SO\textsubscript{2} concentration, relative humidity, gas pressure and current density on SO\textsubscript{2} crossover are discussed. Experimental results reveal that the anode tends to be poisoned heavily with the increasing concentration of SO\textsubscript{2} in the cathode. The coverage of the anode catalyst by SO\textsubscript{2} permeating from the cathode enlarges with the decreasing relative humidity in the anode. The rate of SO\textsubscript{2} crossover from the anode to the cathode is promoted at high current density when SO\textsubscript{2} is directly introduced into the anode side instead of the cathode side, which can be ascribed to the electro-osmotic drag effect. Gas pressures show no obvious effects on SO\textsubscript{2} crossover. A co-permeation mechanism of SO\textsubscript{2} with water is deduced based on the overall analysis.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are usually considered as one of the most promising alternative power sources for transportation and stationary applications due to their high energy efficiency, zero emission and rapid start-up. Ambient air, which always contains impurities (NO\textsubscript{x}, SO\textsubscript{2}, CO, etc.), is commonly used as the cathode oxidant in PEMFCs. Among those impurities, sulfur dioxide (SO\textsubscript{2}) is almost the most deleterious to the performance of PEMFCs [1].

The effect of SO\textsubscript{2} on PEMFC performance has been widely studied. The cell performance decreased by 53% and by 78% after the cell exposure to 2.5 ppm and 5 ppm SO\textsubscript{2}–air mixture, respectively [2]. Jing et al. [3] demonstrated that 35% decay on the cell performance was found when the cell was exposed to 1 ppm SO\textsubscript{2} for 100 h. Moreover, 0.25 ppm SO\textsubscript{2}–air mixture could dramatically degrade the cell performance [4]. The pollution mechanism of SO\textsubscript{2} is also deeply investigated. Most researchers supported that SO\textsubscript{2} occupied the active sites of the catalyst by its adsorption on the platinum catalyst and thus decreased the catalytic activities [2–4]. The modes of SO\textsubscript{2} adsorption on the platinum catalyst were distinguished into linear adsorption and bridged adsorption [5]. Fu et al. [6] investigated the potential dependence of SO\textsubscript{2} poisoning and oxidation. They suggested that SO\textsubscript{2} molecules could be adsorbed on the Pt catalyst without charge transfer at 0.65 V, oxidized above 0.65 V and reduced below it. To date, some methods, such as cycle voltammogram (CV) scans, open circuit voltage (OCV) and I–V measurements, have already been used to handle with SO\textsubscript{2} poisoning [2,7,8]. Additionally, Ma et al. [9] confirmed that activated carbon could be used as air filtration adsorbent to prevent SO\textsubscript{2} from poisoning the cell catalyst.

Degradation of PEMFC performance caused by SO\textsubscript{2} in air is intrinsically due to SO\textsubscript{2} adsorption on the platinum surface of the cathode catalyst. Recently, several researchers have found that some impurities could migrate through the membrane from one side of the cell into the other side and poison the platinum catalyst on the two sides. Qi et al. [10,11] studied the effect of CO in the anode on the performance of the PEMFC cathode. They found that CO could migrate through the membrane to poison the cathode catalyst and cause dramatic performance degradation. It was also reported that H\textsubscript{2}S in hydrogen could pass through the electrolyte membrane, and damage the cathode catalyst [12]. Furthermore, Brosha et al. [13] measured the rates of H\textsubscript{2}S crossover with an ion-probe technique. Under their experimental conditions, the calculated rates of H\textsubscript{2}S crossover varied from 7.58 × 10\textsuperscript{-10} to 4.65 × 10\textsuperscript{-9} g s\textsuperscript{-1} cm\textsuperscript{-2}. The phenomenon of SO\textsubscript{2} crossover in PEMFCs has also been reported in Refs. [14,15]. They found that SO\textsubscript{2} in the cathode could permeate through the membrane into the anode, and poison the catalyst of the two electrodes. Useful results...
have been given in the references mentioned above. However, the mechanism and the influence factors of SO2 crossover still need to be further explored.

In this paper, we implemented detailed studies on the phenomenon of SO2 crossover. CV measurements were performed on both the cathode and the anode to detect behaviors of SO2 poisoning. The mechanism of SO2 crossover was also discussed.

2. Experimental

In this study, all experiments were carried out in a single cell with an active area of 5 cm². A Nafton® 212 membrane (Dupont) was sandwiched by two commercial gas diffusion electrodes (Sunrise Power Co., Ltd.) and hot-pressed to form a membrane-electrode-assembly (MEA). The Pt loadings for both of the cathodic and anodic electrodes were 0.4 mg cm⁻². The parallel flow field was machined on the flexible graphite, and the cell was then tightened using stainless steel endplates, seal rubber, bolts and nuts.

The cell temperature was constantly kept at 70 °C during all experiments. The flow rates of H₂ and air were 50 and 1000 sccm (standard cubic centimeters per minute), respectively. The operating pressure of the anode side was 0.1 MPa. Other parameters, such as relative humidification (RH), the operating pressure of the cathode side (P_air) and SO2 concentration, were adjusted according to the experimental arrangement. Flows of H₂ and air were separately controlled by a mass flow controller (Beijing Sevenstar Electronics Co., Ltd.) fixed at the electrode outlet. The flux of SO₂ was controlled by the mass flow controller at the electrode inlet. SO₂ was mixed with the humidified air or H₂ in order to avoid SO₂ dissolving in water and adsorbing in the humidifier. The schematic diagram of the fuel cell system is shown in Fig. 1.

The single cell was tested with a constant-current mode by SUN-FEL 300 A (Sunrise Power Co., Ltd.). The voltage–time (V–t) curves could be automatically recorded in a computer. Thus, the decay of the voltage could be observed during the continuous injection of SO₂. After the cell was exposed to SO₂ for a certain time, the cyclic voltammetry (CV) measurements were performed by using a PARSTAT 2273 electrochemical station (America, EG&G Instruments Corp.). The applied potential range was from 0.05 to 1.4 V versus dynamic hydrogen electrode (DHE), and the scan rate was 50 mV s⁻¹. During CV experiments, when the cathode (or the anode) was acting as the working electrode with N₂ purging, the anode (or the cathode) was correspondingly acting as the reference and counter electrodes with pure H₂ supply.

3. Results and discussion

3.1. The phenomenon of SO₂ crossover in PEMFCs

Fig. 2 shows the variations of eight CV cycles for both of the cathode and the anode after the cathode side was exposed to 15 ppm SO₂–air mixture at 500 mA cm⁻² for 2 h. The anode was fed with pure hydrogen. During the experiment, the relative humidities in the anode and cathode sides were all kept at 100%, and the pressures of reacting gases in the cathode and the anode were both 0.1 MPa. Fig. 2(a) shows the typical CV curves after SO₂ poisoning the cathode catalyst. It can be seen that the current peak on the first cycle differs from the followings. The current peak of hydrogen-desorption is lower, while that of oxygen oxidation is higher than the corresponding current peaks on the following scans. According to the report in Ref. [6], the reduced hydrogen-desorption peak is attributed to SO₂ adsorption and occupation on active sites of the cathode catalyst. The large oxidation peak is formed when the potential reaches about 1.1 V, at which SO₂ adsorption on
platinum catalyst is electro-oxidized. The corresponding electrochemical reactions are shown in the following equations:

\[ \text{Pt} - \text{SO}_2 + \text{O}_2 \rightarrow 2\text{Pt} - \text{SO}_3 \]  \hfill (1)

\[ \text{Pt} - \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{Pt} + \text{H}_2\text{SO}_4 \]  \hfill (2)

In the subsequent CV cycles, the oxidation peaks of SO\textsubscript{2} disappear and the peaks of hydrogen-desorption reemerge and finally overlap. This also means that all adsorbed SO\textsubscript{2} on the catalyst is removed. According to Refs. [16,17], when adsorbed sulfur species are removed from the platinum catalyst, the voltammogram for the final several CVs of the poisoned catalyst is almost identical to the CV of the fresh catalyst. The final CVs of the poisoned electrode and the CV of the fresh electrode may not fully overlap because of the complex of cells, but they are very close, which could be both observed in Refs. [18,19]. Therefore, the final CV of the poisoned electrode is regarded as the CV of the fresh electrode in the whole text.

Due to the high sensitivity of the platinum catalyst, CV measurements were chosen to detect if there was any SO\textsubscript{2} on the platinum catalyst of the anode. In this operation, the anode was acting as the working electrode with N\textsubscript{2} purging and the cathode as the reference and counting electrodes with pure H\textsubscript{2} supply. Results are shown in Fig. 2(b). From Fig. 2(b), it can be seen that the hydrogen-desorption peak on the first cycle is slightly smaller than that on the subsequent cycles. The inset of Fig. 2(b) clearly shows that there is the distinct difference between the peak areas of hydrogen-desorption on the first cycle and that on the following cycles. Moreover, an additional oxidation peak is observed at about 1.1 V for the anode during the first positive scan. In the following cycles, the additional oxidation peaks disappear, and the hydrogen-desorption peaks almost overlap. These results indicate that the active sites of the anode catalyst are occupied by some impurity.

By comparing Fig. 2(b) with Fig. 2(a), it indicates that characters of CV curves of the anode are similar to that of the cathode. The hydrogen-desorption peaks on the first cycle at both of the anode and the cathode are smaller than that on the following cycles. An additional peak caused by the oxidation of some impurity appears at a potential of about 1.1 V on the first cycle, and disappears in the subsequent cycles. Then the corresponding peaks almost overlap with each other.

Fig. 3 shows the variations of eight cyclic voltammetry curves of the anode after the cathode exposure to 1 ppm SO\textsubscript{2}–air for 10 h at 500 mA cm\textsuperscript{-2}. Operating pressure: \( P_{\text{air}} = 0.1 \text{ MPa} \); humidification temperatures of the anode and cathode: 70 °C and 70 °C.

Due to the high sensitivity of the platinum catalyst, CV measurements were chosen to detect if there was any SO\textsubscript{2} on the platinum catalyst. In this operation, the anode was acting as the working electrode with N\textsubscript{2} purging and the cathode as the reference and counting electrodes with pure H\textsubscript{2} supply. Results are shown in Fig. 2(b). From Fig. 2(b), it can be seen that the hydrogen-desorption peak on the first cycle is slightly smaller than that on the subsequent cycles. The inset of Fig. 2(b) clearly shows that there is the distinct difference between the peak areas of hydrogen-desorption on the first cycle and that on the following cycles. Moreover, an additional oxidation peak is observed at about 1.1 V for the anode during the first positive scan. In the following cycles, the additional oxidation peaks disappear, and the hydrogen-desorption peaks almost overlap. These results indicate that the active sites of the anode catalyst are occupied by some impurity.

By comparing Fig. 2(b) with Fig. 2(a), it indicates that characters of CV curves of the anode are similar to that of the cathode. The hydrogen-desorption peaks on the first cycle at both of the anode and the cathode are smaller than that on the following cycles. An additional peak caused by the oxidation of some impurity appears at a potential of about 1.1 V on the first cycle, and disappears in the subsequent cycles. Then the corresponding peaks almost overlap with each other. Because SO\textsubscript{2} in the cathode is the only impurity during the whole experiment, it can be concluded that the impurity adsorbed on the anode catalyst could be SO\textsubscript{2}, which migrates from the cathode side to the anode side.

Fig. 3 shows the variations of eight cyclic voltammetry curves of the anode after the cathode exposure to 1 ppm SO\textsubscript{2}–air mixture at a current density of 500 mA cm\textsuperscript{-2} for 10 h. The results are similar to that of the cathode exposure to 1 ppm SO\textsubscript{2}–air mixture. It can be seen that the hydrogen-desorption peak on the first cycle is smaller than that on the subsequent cycles, and an additional oxidation peak appears at a potential of about 1.1 V. With the increase in the CV cycles, the oxidation peaks become smaller and the hydrogen-desorption peaks become larger. It indicates that even if the concentration of SO\textsubscript{2} in air is extremely low, SO\textsubscript{2} can still pass through the electrolyte membrane to the anode and poison the anode catalyst.

3.2. SO\textsubscript{2} crossover in PEMFCs under various conditions

3.2.1. Effect of the relative humidity (RH) difference between the anode and the cathode on SO\textsubscript{2} crossover

The pressures of the cathode and the anode sides were both kept at 0.1 MPa. 15 ppm SO\textsubscript{2}–air mixture was supplied into the cathode. Working electrode with N\textsubscript{2} purging and the cathode as the reference and counting electrodes with pure H\textsubscript{2} supply. Results are shown in Fig. 2(b). From Fig. 2(b), it can be seen that the hydrogen-desorption peak on the first cycle is slightly smaller than that on the subsequent cycles. The inset of Fig. 2(b) clearly shows that there is the distinct difference between the peak areas of hydrogen-desorption on the first cycle and that on the following cycles. Moreover, an additional oxidation peak is observed at about 1.1 V for the anode during the first positive scan. In the following cycles, the additional oxidation peaks disappear, and the hydrogen-desorption peaks almost overlap. These results indicate that the active sites of the anode catalyst are occupied by some impurity.

By comparing Fig. 2(b) with Fig. 2(a), it indicates that characters of CV curves of the anode are similar to that of the cathode. The hydrogen-desorption peaks on the first cycle at both of the anode and the cathode are smaller than that on the following cycles. An additional peak caused by the oxidation of some impurity appears at a potential of about 1.1 V on the first cycle, and disappears in the subsequent cycles. Then the corresponding peaks almost overlap with each other. Because SO\textsubscript{2} in the cathode is the only impurity during the whole experiment, it can be concluded that the impurity adsorbed on the anode catalyst could be SO\textsubscript{2}, which migrates from the cathode side to the anode side.

3.2.2. Effect of the relative humidity (RH) difference between the anode and the cathode on SO\textsubscript{2} crossover

The pressures of the cathode and the anode sides were both kept at 0.1 MPa. 15 ppm SO\textsubscript{2}–air mixture was supplied into the cathode at 500 mA cm\textsuperscript{-2}. The humidity levels in the cathode and the anode (expressed as rRH and dRH) were 100% and 14%, respectively. After the cell was poisoned by SO\textsubscript{2} for 2 h, eight CV cycles were carried out for the anode. CV curves on the first and the eighth cycles are shown in Fig. 4(a). From Fig. 4(a), it can be observed that the hydrogen-desorption peak on the first cycle is smaller than that on the eighth cycle, which means that SO\textsubscript{2} migrates through the membrane into the anode side and occupies the Pt active sites.

The oxidation peak on the first cycle is bigger than that on the eighth cycle at the potential of about 1.1 V, which indicates that the impurity is electro-oxidized at this potential. Finally, the hydrogen-desorption peaks recover and the SO\textsubscript{2} oxidation peaks diminish gradually in the sequential CV cycles. Fig. 4(b) shows the CV curves of the anode side where dRH and cRH were both 100%. Similar results are obtained. The ratio of the hydrogen-desorption peak area on the first cycle to that on the eighth cycle is expressed as Eq. (3):

\[ \frac{\theta_H}{\theta_{H1}} = \frac{\theta_{H1}}{\theta_{H8}} \]  \hfill (3)

In this equation, \( \theta_{H1} \) is the hydrogen-desorption peak area on the first cycle, \( \theta_{H8} \) is the hydrogen-desorption peak area on the eighth cycle. Therefore, \( \theta_H \) may denote the active sites of the platinum catalyst for hydrogen desorption after the cell is poisoned. Correspondingly, SO\textsubscript{2} coverage of the catalyst can be expressed as Eq. (4):

\[ \theta_{\text{poisoning}} = 1 - \theta_H \]  \hfill (4)

Here, \( \theta_{\text{poisoning}} \) denotes the coverage of SO\textsubscript{2} on the platinum catalyst. In the case of \( \text{dRH} = \text{cRH} = 100\% \), \( \theta_H \) is equal to 98%, which indicates that the \( \theta_{\text{poisoning}} \) is 2%. In the case of \( \text{dRH} (14\%) < \text{cRH} (100\%) \), \( \theta_H \) is equal to 76%, which indicates that \( \theta_{\text{poisoning}} \) is 24%. Therefore, the anode catalyst is more severely poisoned in the latter case. Under the condition of \( \text{dRH} < \text{cRH} \), the relative humidity in the anode is lower than that in the cathode, so water transport is promoted from the cathode to the anode across the electrolyte membrane due to back diffusion. The water transport also assists SO\textsubscript{2} migrating from the cathode to the anode, which leads to a more severe contamination in the anode catalyst.

Fig. 5 shows the comparison of CV curves on the first cycle after the cell was poisoned by SO\textsubscript{2} under different humidification conditions. From Fig. 5, it can be seen clearly that more platinum active sites of the anode catalyst are occupied by SO\textsubscript{2} when the relative humidity in the anode is lower than that in the cathode. The crossover rate of SO\textsubscript{2} is proportional to the difference of the relative humidity between the cathode and the anode.
As it is well known, SO₂ can easily dissolve in water with a volume ratio of 40:1. Thus, the majority of SO₂ dissolves in water. A portion of SO₂ dissolved in water adsorbs on the catalyst surface, and the rest transports to the other side accompanying with water. As a result, the dissolution of SO₂ plays a role in assisting SO₂ migration.

3.2.2. Effect of gas pressures on SO₂ crossover

The relative humidities in both the anode and the cathode were kept at 100%. The anode pressure was kept at 0.1 MPa, while the cathode pressure was adjusted to 0.1 MPa, 0.14 MPa and 0.18 MPa. 15 ppm SO₂–air mixture was fed into the cathode at a current density of 500 mA cm⁻² for 2 h. CV scans were performed on the anode after the cell was poisoned. θ_H₂ and θ_poisoning were calculated and summarized in Table 1. From Table 1, it can be seen that θ_H₂ is 98%, 87% and 80% under the SO₂ concentrations of 15 ppm, 20 ppm and 30 ppm, respectively. Thus, the coverage of the anode catalyst, θ_poisoning, is 2%, 13% and 20%, respectively. The higher the SO₂ concentration is, the higher the coverage of SO₂ is. The anode catalyst is more and more severely deteriorated with the increase in SO₂ concentrations, which points out that more SO₂ permeates across the membrane from the cathode into the anode. SO₂ crossover rate is proportional to the concentration and the cathode had little influence on water transport, which was previously reported by Chai et al. [20].

3.2.3. Effect of SO₂ concentrations on SO₂ crossover

The cathode pressure was kept at 0.1 MPa. cRH and aRH were all 100%. SO₂ in air with different concentrations was fed into the cathode at a current density of 500 mA cm⁻² for 2 h. CV scans were performed on the anode after the cell was poisoned. θ_H₂ and θ_poisoning were calculated and summarized in Table 1. From Table 1, it can be seen that θ_H₂ is 98%, 87% and 80% under the SO₂ concentrations of 15 ppm, 20 ppm and 30 ppm, respectively. Thus, the coverage of the anode catalyst, θ_poisoning, is 2%, 13% and 20%, respectively. The higher the SO₂ concentration is, the higher the coverage of SO₂ is. The anode catalyst is more and more severely deteriorated with the increase in SO₂ concentrations, which points out that more SO₂ permeates across the membrane from the cathode into the anode. SO₂ crossover rate is proportional to the concentration and the cathode had little influence on water transport, which was previously reported by Chai et al. [20].
Table 1
Effect of SO₂ with different concentrations on SO₂ crossover.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ₂ (%)</td>
<td>98</td>
<td>87</td>
<td>80</td>
</tr>
<tr>
<td>θ₂ poisoning (%)</td>
<td>2</td>
<td>13</td>
<td>20</td>
</tr>
</tbody>
</table>

gradient. The concentration should be related to the concentration of SO₂ in water due to the dissolution of SO₂.

3.2.4. Effect of the electro-osmotic drag on SO₂ crossover

Another factor, which influences the water transport, is the electro-osmotic drag (water molecules are dragged by protons migrating from the anode to the cathode). Based on this point, a special experiment was carried out by directly supplying SO₂ into the anode side. 15 ppm SO₂-H₂ mixture was fed into the anode at different current densities for 2 h. The relative humidities in the anode and the cathode were all 100%. The pressures in the anode and the cathode were both kept at 0.1 MPa. CV scans were performed on the cathode after the cell was poisoned.

Fig. 7 shows the CV curves of the cathode obtained after the cell ran at 500 mA cm⁻². The insert is the enlarged section of the hydrogen-desorption peaks on the first cycle and the eighth cycle. From the insert, it is clearly observed that the hydrogen-desorption peak on the first cycle is smaller than that on the eighth cycle. It indicates that a part of active sites of the cathode catalyst are occupied by some impurity. When the scan potential gets more positive, a tiny additional current appears at about 1.1 V, which is caused by the electro-oxidization of the impurity. As it is known, SO₂ in H₂ is the only impurity in the whole experiment. Therefore, the impurity adsorbed on the cathode catalyst can be only the impurity of SO₂ which migrates from the anode. Under this condition, θ₂H is 90%, which indicates that 10% active sites of the cathode catalyst are covered by SO₂ migrating from the anode. Fig. 8 shows the CV curves of the cathode obtained after the cell ran at 1000 mA cm⁻². Under this condition, θ₂H is about 78%. Correspondingly, the coverage of SO₂ is about 22%. Obviously, the cathode catalyst is more severely contaminated by SO₂ from the anode under the condition of higher current density. As it is known, more water transports from the anode to the cathode due to the electro-osmotic drag when the cell is operated at a higher current density. Therefore, more SO₂ dissolves in water and permeates into the cathode from the anode.

From all the experiments above, it can be concluded that SO₂ mainly transports through the membrane via water. It means that the mechanism of SO₂ crossover might be a co-permeation mechanism of SO₂ with water. The sketch of the supposed mechanism is described in Fig. 9. SO₂ arrives at the catalyst layer of MEA through the gas diffusion layer. A portion of that adsorbs on the catalyst surface, and the rest migrates across the electrolyte membrane together with water into the other side of MEA.

In the present study, we mainly paid attention to the behaviors of SO₂ crossover and tried to explore the mechanism of SO₂ crossover. The accurate rate of SO₂ crossover and how SO₂ crossover affects the anode overpotential will be the focus of our future work.

Fig. 7. Cyclic voltammograms of the cathode obtained after the anode exposure to 15 ppm SO₂-H₂ with for 2 h when the cell ran at 500 mA cm⁻². Operating pressure: $P_{air} = P_{H₂} = 0.1$ MPa; humidification temperatures of the anode and cathode: 70 °C and 70 °C. The insert is the enlarged part of CV curves of hydrogen peaks on the first cycle and on the eighth.

Fig. 8. Cyclic voltammograms of the cathode obtained after the anode exposure to 15 ppm SO₂-H₂ for 2 h when the cell ran at current density of 1000 mA cm⁻². Operating pressure: $P_{air} = P_{H₂} = 0.1$ MPa; humidification temperatures of the anode and the cathode: 70 °C and 70 °C.

Fig. 9. Sketch of the mechanism of SO₂ crossover: co-permeation with water.
4. Conclusions

The phenomenon of SO₂ crossover in PEMFCs was studied. SO₂ in air could migrate across the membrane from the cathode to the anode, adsorb on the anode catalyst and occupy the active sites. The phenomenon of SO₂ crossover even occurred in the presence of trace amount of about 1 ppm. SO₂ crossover depended on various conditions including relative humidity, concentration gradient and current density, while gas pressures had no obvious effect on it. When the relative humidity in the anode was lower than that in the cathode, more active sites of the anode catalyst would be covered by SO₂ from the cathode. The coverage of the anode catalyst was 2%, 13% and 20% under the SO₂ concentrations of 15 ppm, 20 ppm and 30 ppm, respectively. It indicated that the anode catalyst was more seriously contaminated with an increase in SO₂ concentration in the cathode side. When SO₂ was directly fed into the anode, SO₂ crossover rate was higher at 1000 mA cm⁻² than that at 500 mA cm⁻². This was because more water molecules passed through the membrane into the cathode by the electro-osmotic drag, and it led to a more serious SO₂ crossover by SO₂ dissolution in water. Thus, it was concluded that the SO₂ crossover mechanism could be the co-permeation of SO₂ with water.

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