Direct Formation of Metal Layer on Anion Exchange Membrane Using Electroless Deposition Process

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Abstract

In this work, a novel electroless deposition process on the anion exchange membrane (AEM) is proposed. AEM surface has a positively charged functional group, which in general do not allow the catalyst particle, such as Pt, Pd to be formed on the surface. Hence, a different strategy from the conventional catalyzation process was required. We found that the sensitization process using Sn-containing solution, which is widely applied in the electroless plating on nonconductive substrates, hindered the Pd particle modification, which hence inhibited the following deposition reaction. Our several experiments and density functional theory analyses suggest that for Pd particle modification, anion in the bath turned out to play a key role. In particular, Cl− provides the sufficiently strong connection between the precursor PdCl2 and positive functional group of the substrate. This leads to favorable deposition of Pd catalyst particles and metal layer formation on the AEM. Therefore, we conclude that just a single pre-treatment to immerse the AEM films into PdCl2/HCl solution is capable to perform electroless plating on it. We applied the novel process to the electrode formation, such as Pt and Ni, on the AEM for hydrogen evolution reaction (HER) as a case study. Both Pt and Ni-P was successfully formed on the AEM. The electrochemical measurements show that those electrodes are able to serve as the catalytic electrode for HER. The electroless process proposed here opens possibility of the direct metal fabrication on ion exchange membrane surface.

Keywords: Electroless Deposition, Catalyzation Process, Anion Exchange Membrane

1. Introduction

Electroless deposition is a powerful technique to fabricate functional thin films on non-conductive substrates.1–4 The process uses no external power, and so it requires a pre-treatment to provide on the substrates catalyst nuclei that initiate the reaction of reducing agent as electron sources.5,6 This leads to the reduction of the metal cations and thin films formation selectively promoted on the surface of glass, ceramics, as well as plastics. It is expected that the plating technique becomes available to as many types of non-conductive as possible. And for this, a variety of catalyzation process prior to the deposition is needed to be developed, because it is very critical to determine physical, geometrical, and chemical properties of the deposits.

For example, direct formation of metal thin films on polymer membranes, such as ion exchange membrane has a potential to be utilized in many applications.3,7 In these days, anion exchange membrane (AEM) has emerged as an important component of electrochemical energy devices.7,8 In particular in a water electrolysis devise, it works as a membrane of OH− pathway between the anode side and cathode side, which makes possible to conduct cost-effective alkaline water electrolysis. One of the effective ways to implement the AEM into the device is the direct preparation of electrode materials for the electrolysis reaction on the AEM.10,11 Our previous studies proposed the fabrication process of AEM with the electrode attached on, by using the ionomer. It turned out that the electrode-covered AEM provided good cell performance because it lowers a resistance between the different types of catalyzation pre-treatment were applied: one is the conventional process using the Sn solution and the Pd solution called the sensitizing-activation process (Sn–Pd process hereafter), while the other is modified one based on the Sn–Pd process. In the
Sn–Pd process, AEM was immersed in 44 mmol dm$^{-3}$ SnCl$_2$ (UGR grade, Kanto Chemical Co.) containing HCl (UGR Grade, Kanto Chemical Co.) solution, after that, in 10 mM PdCl$_2$ (UGR grade, Kanto Chemical Co.) contained HCl solution (EL Grade, Kanto Chemical Co.) for 30 s each. After each step, AEM was rinsed by deionized water for 15 s. The above process was repeated 3 times. After this pre-treatment process, AEM was immersed in the bath containing 50 mM dimethylamine borane (DMAB, Regent Grade, Tokyo Chemical Industry Co.), which is expected to enhance the HER performance of Ni–P on AEM in the size of 10 mm × 10 mm were utilized as the cathodes. The anode was Ni foam (10 mm × 10 mm, Nagamine Manufacturing) that is practically employed in alkaline water electrolysis scheme. The electrochemical measurements were performed by employing membrane electrode assembly (MEA) structure. The geometric electrode area of both cathode and anode are 10 × 10 mm$^2$, which are stacked parallelly with the gasket put between those two. Furthermore, the electrode stack is put between the two current collecting plates. Each plate has a flow channel that runs parallel to the electrode surface. The electrolyte is supplied from the flow field. The MEA assembly is particularly provided by the measurement cell designed by Yokohama National University. The cell structure of the similar concept is schematically described elsewhere.$^{27}$ One of the biggest advantages of the cell is the spring behind the electrode on one side, which allows us to standardize the pressure for the stack of electrodes. The electrolyte for water electrolysis was 1.0 M K$_2$CO$_3$ solution. Prior to the measurements, the K$_2$CO$_3$ electrolyte was purged by N$_2$ gas for 20 min to remove the dissolved oxygen. The electrolyte flow was introduced by a smooth-flow pump (Q-100-TT-P-S, Takumina Co.) only to the anode side from the inlet at the bottom of the cell to the outlet at the upper, based on the previous study.$^{13,14}$ The flow rate was 5.0 mL min$^{-1}$. The detailed setup conditions of the electrochemical measurement cell are shown in Table 3. The linear sweep voltammetry was performed by the two-electrodes system with sweeping the voltage range from open circuit voltage (OCV) to −2.5 V with a scan rate of 10 mV s$^{-1}$. The galvanostatic electrolysis at −500 mA cm$^{-2}$ for 10 min was also carried out.

3. Results and Discussion

3.1 Electroless deposition process on AEM

In order to explore the suitable catalyzation process for the electroless Ni–P deposition on AEM, Sn–Pd process was applied at first. Figures 2(a) and 2(b) show AEM films before and after the electroless Ni–P deposition process.
catalyzed, respectively. The color of the AEM surface changes from white color (Fig. 2(a)) to brown (Fig. 2(b)) during the Sn–Pd process. However, even after this, Ni–P layer was not formed on the AEM in the electroless deposition bath. We suspected that the deposition and/or adsorption species by the immersion into the Sn bath somehow hindered the Pd nuclei formation on the films. Thus, we immersed the AEM into the Pd bath without any pre-processes, such as Sn bath immersion. In contrast with the case of the conventional Sn–Pd process, Ni–P layer is successively formed by the single immersion process omitting Sn bath (Pd process hereafter). Though little change in the AEM surface is observed after Pd process (Fig. 2(c)), Ni–P layer clearly covers the whole surface of AEM (Fig. 2(d)). These results indicate that Ni–P layer is not formed on AEM when it is immersed into the Sn solution as the catalyzation process.

Figure 3 shows the SEM images of Ni–P on AEM. Particle-like morphologies that are often seen in the case of Ni–P electroless deposition are observed on the entire AEM surface (Fig. 3(a)). The cross-sectional SEM image demonstrates that Ni–P layer on AEM has compact and dense structures (Fig. 3(b)).

3.2 Theoretical analysis of the interaction between AEM and chemical species in the catalyzation process

In order to analyze the catalyzation pathway during both Sn–Pd and Pd processes, DFT calculation was carried out. Presuming from the experimental results obtained in the last section, Sn bath immersion would provide some species poisoning the adsorption site for the Pd precursor. The assumption requires to analyze the interaction between AEM and Sn-related species. Furthermore, a question remains on why only Pd bath immersion made possible to perform electroless Ni–P deposition. This also requires the theoretical analyses for interaction between AEM and Pd-related species.

Previous studies indicated that the functional group in the side chain had a significant influence on the interaction with the chemical species during the reaction. On the contrary, the carbon chain itself is inert to the chemical bond formation with other species, and thus we assume their effects negligible. Another past study as to the chemical structure of proton exchange membrane (PEM) proposed that the functional groups in the side chains are randomly located. Based on the model, the calculation model was composed of only several trimethyl ammonium assumed to come randomly from surrounding branches around Sn- or Pd-related species, in order to evaluate the interaction energy among them. Here we focus on investigating the interaction between Sn/Pd species and the quaternary ammonium functional group on the AEM surface.

Figure 4 shows the optimized structures of the interaction between AEM and Sn, Pd species. The Sn species in the Sn–Pd process was assumed as SnO₃²⁻, which is obtained by the reaction in Eq. (1) from the previous study. The equilibrium structures in Fig. 4(a) demonstrates the O atom in SnO₃²⁻ interacts with the CH₄ groups in the trimethyl ammonium group. The interaction energy between SnO₃²⁻ and the trimethyl ammonium group is −55.37 kJ mol⁻¹, indicating that SnO₃²⁻ strongly interacts with AEM after the Sn–Pd process. In the case of the Pd process, [PdCl₄]²⁻ is the most predominant as Pd species in the solution and it shows interaction with the CH₄ groups. The interaction energy calculated from the optimized structures in Fig. 4(b) is −20.67 kJ mol⁻¹. These results indicate that the interaction between AEM and [PdCl₄]²⁻ is not so weak, suggesting that the Pd species is stably located near the AEM, and [PdCl₄]²⁻ is transformed into the catalyst particle of the following electroless deposition. The Mulliken charge analyses indicate that those interaction is not necessarily chemical coordination bond, but electrostatic effect. This is attributed to strongly negative charge of O in SnO₃²⁻ and of Cl in [PdCl₄]²⁻. However, the value of the interaction energy between SnO₃²⁻ and AEM is larger than that of between [PdCl₄]²⁻ and AEM, indicating that SnO₃²⁻ interacts with AEM stronger than [PdCl₄]²⁻. The SnO₃²⁻ species is considered to suppress Pd particle formation, which corresponds to the past study. These analyses provide the molecular level pathway of catalyzation process: Cl⁻ ion becomes a crosslink between Pd precursor cation and the functional group of AEM surface and it results in Pd catalyst nuclei formation after the immersion into Pd bath, whereas the Sn bath immersion prior to the Pd bath delivers Sn species that are oxidized to SnO₃²⁻ through Pd bath immersion and it dominates the adsorption site for Pd, resulting in no electroless deposition observed.

Figure 2. Observation results of AEM: (a) before the electroless deposition process, (b) after the Sn–Pd process, (c) the Pd process, and (d) the Ni–P electroless deposition.

Figure 3. SEM images of prepared Ni–P on AEM from (a) top view and (b) cross-sectional view.
3.3 Evaluation of the HER performance of prepared catalytic electrodes in AEM water electrolysis

In order to evaluate HER performance of the prepared catalytic electrodes during AEM water electrolysis process, the electrochemical measurements were carried out. Before the electrochemical measurements, Pt catalytic electrodes fabricated by the electroless deposition and Pt/C catalysts fabricated by the spray process based on the previous studies were prepared as controlling samples.

Figure 5 shows SEM images of the electrolessly deposited Pt on AEM; the uniform deposition is observed on the entire surface, and its morphologies corresponds to the previous study. SEM images also prove that the compact layer is formed on AEM surface and the thickness of Pt electrode is approximately 2.0 µm.

Linear sweep voltammetry (LSV) of electroless Ni–P, Pt, and Pt/C were performed by sweeping the voltage from the OCV to −2.5 V with a scan rate of 10 mV s⁻¹ (Fig. 6(a)). It shows that the current density increases in all electrodes as the voltage application proceeds, indicating that both Ni–P and Pt layer function as the catalytic electrode for HER. The onset voltage of Ni–P electrode is negatively larger than that of Pt electrode due to lower inherent HER activity of Ni–P. The value of the current density of both electroless Pt and Pt/C electrodes are almost the same at −2.5 V. On the other hand, multiple peaks appear in the LSV with Pt/C. Previous studies reported that Pt/C suffered from the dissolution in the electrolyte under strongly alkaline conditions. The Pourbaix diagram also indicated that C was dissolved to be

Figure 4. Equilibrium structures of the interaction between AEM surface and (a) the Sn species and (b) the Pd species in the catalyzation process.

Figure 5. SEM images of the prepared Pt on AEM by the electroless deposition process from (a) top and (b) cross-sectional view.

Figure 6. Electrochemical measurement results of prepared Ni–P, Pt and Pt/C electrodes: (a) linear sweep voltammogram of prepared electrodes (scan rate −10 mV s⁻¹) and (b) chronopotentiogram during the galvanostatic electrolysis at −500 mA cm⁻² for 10 min with different electrodes.
4. Conclusion

This study achieved the electroless deposition of metal layer on AEM by developing a new pre-treatment process to catalyze the membrane surface. It turned out that Sn–Pd process that is widely applied as the sensitizing-activation pre-treatment inhibited the following electroless process to form metal layer especially in the case of AEM. DFT analysis indicates that strong interaction between Sn/Pd and the functional group of AEM surface emerges to hinder the following Pd catalyst nuclei formation. On the other hand, just a single process that involves only immersion into Pd-containing bath allowed us to modify Pd particles as catalyst nuclei, which led to the achievement of metal formation on the AEM surface. This is due to sufficiently strong interaction between the catalyst precursor, \( \text{PdCl}_2 \) and trimethyl ammonium on the AEM surface. Because the Pd\(^{2+} \) cation alone should not interact strongly with positively charged quaternary ammonium functional group, Cl\(^- \) between them is expected to play a key role to set the adsorption structure stable. The novel method was applied to the electrode formation on the AEM for alkaline water electrolysis. The electrochemical measurements prove that those for HER show acceptable catalytic performances. Those results lead us to conclude that controlling the interaction between the catalyst precursor and the functional group of the AEM surface by tuning anion species to bridge them is one of the key factors to achieve the electroless deposition on AEM. This will expand the potential of the electroless deposition process in the industrial field of new generation energy devices.

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