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ARTICLE

Cr effect on the durability of Pt-TM catalysts for PEMFCs

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Pt-TM-Cr/C alloy catalysts were prepared using a polyol method to improve their durability through the addition of a small amount of Cr, which is expected to prevent dissolution of transition metal (TM). $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and CrCl_2 were used as precursors. X-ray diffraction was used to determine the compositions and sizes of the prepared electrocatalysts. The average sizes of the electrocatalyst particles were estimated to be 2 ~ 4 nm using the Scherrer formula. Transmission electron microscopy observations revealed that the nanoparticles were uniformly distributed on the carbon, i.e., Vulcan XC 72. The durability of the Pt-TM-Cr/C alloy catalysts was evaluated using a cell test and the accelerated durability test. According to the cell tests, Pt-TM(Co)-Cr(67:23:10)/C alloy catalysts are more durable than Pt-TM(Co)/C alloy catalysts. The accelerated stability tests showed that Cr prevents the dissolution of transition metals, which are integral to the durability of the electrode.

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) have received considerable attention for transportation applications, distributed generation, and portable applications due to their high energy density, relatively low operating temperature, low emission of pollutants, and minimal corrosion problems [1-3]. However, the commercial application of PEMFCs is still hindered by several problems including the high cost of the cell components and degradation of cell performance. Specifically, Pt is relatively expensive and is the main component of the electrocatalysts, which raises the production cost. Accordingly, binary alloy catalysts have been widely researched to reduce the amount of Pt required [4-7]. Moreover, durability limitation is a primary problem in commercializing PEMFCs and it has recently been recognized as a vital issue that needs to be addressed before commercialization of PEMFCs can proceed[8].

Binary Pt-alloy electrocatalysts contain transition metals such as Co, Ni, and Ru [9-13]. However, these transition metals dissolve in the acidic environments that PEMFCs operate under. According to Meyers and Darling *et al.*, the transition metals of the catalysts dissolve into the cell and affect the electrode performance and stability [14, 15]. To protect against dissolution of the catalysts, replaced support material [16], water-fluxing [17], pre-leaching [18], and

additives [19] have been investigated. Houa and Shao *et al.* investigated the stability of a bipolar plate coated with CrN/Cr multilayers for PEMFCs [20]. Cr is very stable in acidic environments and is suitable for the operating environment of PEMFCs. However, this coating method requires extra process steps, which incur additional costs, and hence, an alternative method is necessary. One proposal is the addition of Cr to the alloy catalysts, which is expected to prevent dissolution of the transition metal[21-23]. Therefore, ternary Pt-alloy electrocatalysts such as Pt-transition metal (TM)-Cr (where TM = Co or Ni) have attracted significant attention as candidates for high-performance cathode catalysts that will increase the power density, reduce the cost of PEMFC components, and improve the durability of the catalyst.

In this study, Pt-TM-Cr/C alloy electrocatalysts were prepared using a modified polyol method with ethylene glycol or diethylene glycol as the reducing agent and solvent. This method enables accurate control of the size distribution and shape of the particles from the micrometric to colloidal scale. The Cr-containing ternary electrocatalyst was produced with an adequate size and size distribution using this method. Increased durability as a result of the addition of Cr was confirmed via unit-cell tests and long-term stability tests.

2. Experimental procedure

Pt-TM-Cr/C alloy electrocatalysts were prepared by a modified polyol method using 20 wt.% Pt-TM-Cr alloy. In this study, the TM was either Co or Ni. For the synthesis, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich), and CrCl_2 (Aldrich) were used as precursors. Ethylene glycol (EG, Duksan) or diethylene glycol (DEG, Duksan) were used as both reducing agent and solvent. For the purpose of this study, various amounts of Cr (5, 10, or 15 wt.%) were added to Pt/TM solutions which may have molar ratio of 3:1 or 1:1. Fig. 1 shows a flow chart of the preparation procedure. A 0.01 M stock solution of each metallic salt (i.e., Co or Ni, Pt, and Cr) was prepared by dissolving the appropriate salt in the solvent; these stock solutions were required to avoid potential experimental errors in weighing the metallic salts, which are known to be highly hygroscopic.

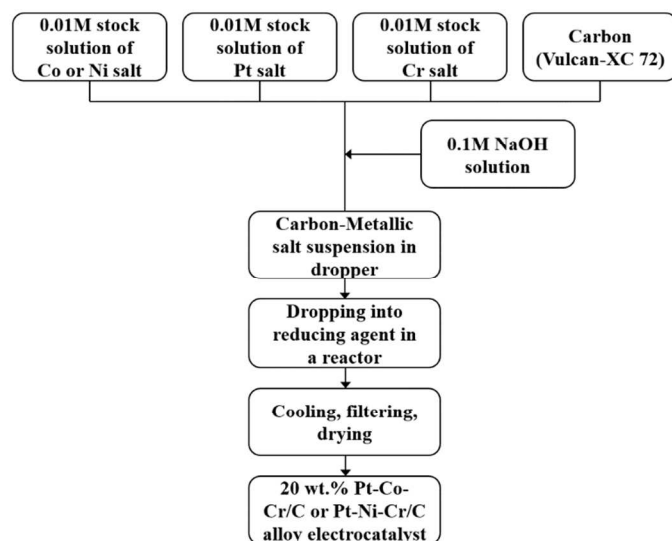


Fig. 1. Procedure for fabrication of catalysts.

The phases of the prepared electrocatalysts were identified using X-ray diffraction (XRD, Rigaku D/MAX- γ B, Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). The XRD patterns were also used to estimate the particle sizes of the electrocatalysts according to the Scherrer formula. Transmission electron microscopy (TEM; JEOL JEM-2010) at an acceleration voltage of 200 kV was used to determine how uniformly the catalyst particles were dispersed on the carbon support and confirm the particle sizes estimated from the XRD data. Additionally, energy dispersive X-ray spectroscopy (EDS) using a beam size of 20 nm was coupled with TEM and inductively coupled plasma atomic emission spectroscopy (ICP-AES; Jobin Yvon JY138 Ultrac) to analyze the

compositions of the electrocatalysts. ICP-AES was also used to examine the metallic residue in the filtrate.

A membrane electrode assembly (MEA) with an active area of 5 cm^2 was fabricated by hot pressing. The anode and cathode were arranged with an interlayer of Nafion 212 pretreated with H_2O_2 and H_2SO_4 solutions and sandwiched between them followed by hot pressing at 170 kg-f/cm^2 and 140°C for 90 s. The unit-cell test was performed at 80°C under atmospheric pressure using H_2 and O_2 as the fuel and oxidant, respectively. The Nafion ionomer loadings were 0.5 mg/cm^2 for the inside of the catalyst layer. And the electrode was loaded 0.4 mg/cm^2 of alloy electrocatalysts.

Stability testing was performed for 100 h of cell operation. Each cathode was coated with four different catalysts, i.e., Pt/C, Pt-Co-Cr (67:23:10)/C, Pt-Co-Cr (45:45:10)/C and Pt-Ni-Cr (67:23:10)/C. During the accelerated stability tests, the voltage was maintained at 0.6 V and the unit cells were kept with temperature of 90°C which is higher temperature than that of normal PEMFC operation ($70\sim 80^\circ\text{C}$).

3. Results and discussion

3.1. Characterization of Pt-TM-Cr/C alloy electrocatalysts

The atomic composition of the Pt-TM-Cr electrocatalyst was analyzed by EDS. The filtrate was analyzed via ICP-AES to confirm the absence of metallic residue. The composition of the catalyst was 73.93 at.% Pt, 22.97 at.% Co, and 3.10 at.% Cr, which differs from the initial composition of 67:23:10. This result indicates that small amounts of Co and Cr were produced, which is likely caused by the different reduction rates of the metal ions in the modified polyol process.

The XRD patterns of the Pt-Ni-Cr/C and Pt-Co-Cr/C electrocatalysts prepared using the modified polyol method with diethylene glycol as the solvent are shown in Figs. 2. Both patterns look similar and consist of three broad peaks at 2θ of $\sim 40^\circ$, $\sim 47^\circ$ and $\sim 68^\circ$, which are superimposed on a diffuse pattern from amorphous carbon with a main peak at 2θ of $\sim 25^\circ$. The three peaks correspond to Pt (111), Pt (200), and Pt (220), respectively. However, these peaks, are at slightly higher angles than those expected for Pt (JCPDS #040802), and there are no additional peaks and shoulders as shown in Figs. 2. These results indicates that smaller Co (or Ni) and Cr atoms were dissolved in a matrix of larger Pt atoms to generate a Pt-TM (Co or Ni)-Cr alloy [24].

Using the Scherrer formula, the average sizes of the electrocatalyst particles were estimated to be $2 \sim 4 \text{ nm}$; these values were confirmed by TEM. The TEM images indicated

that the nanoparticles were distributed uniformly on the carbon, i.e., Vulcan XC-72. Figs. 3(a) and (b) show TEM images of Pt-Co-Cr/C alloy catalysts with Pt/Co/Cr molar ratios of 67:23:10 and 45:45:10, respectively. The average particle sizes of the electrocatalysts were measured and averaged to be 2.24 and 2.12 nm, respectively. For the Pt-Ni-Cr alloy catalysts, the average particle size was 2.43 nm, which is larger than that of the Co alloy catalysts, as shown in Fig. 4. In general, the particle sizes of both electrocatalysts in the PEMFCs is 2 ~ 5 nm, which satisfies the criteria for commercial electrocatalysts [25-27].

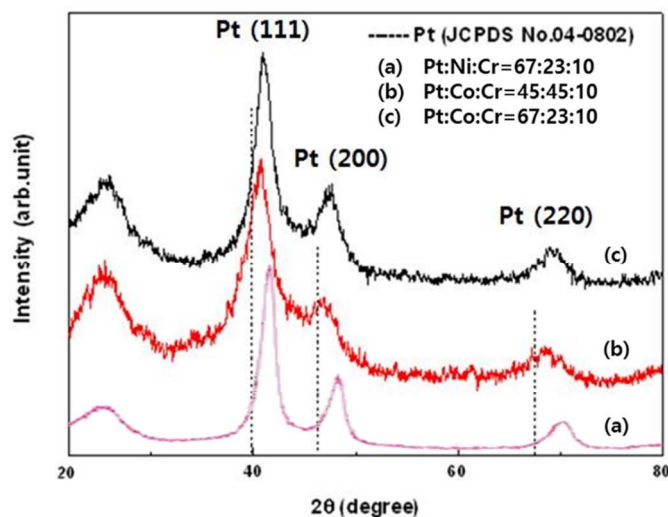


Fig. 2. XRD patterns of (a) Pt-Ni-Cr (67:23:10)/C, (b) Pt-Co-Cr (45:45:10)/C and (c) Pt-Co-Cr (67:23:10)/C.

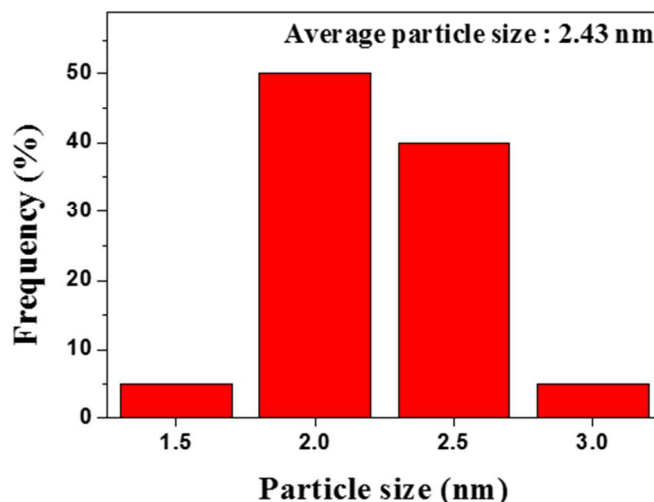
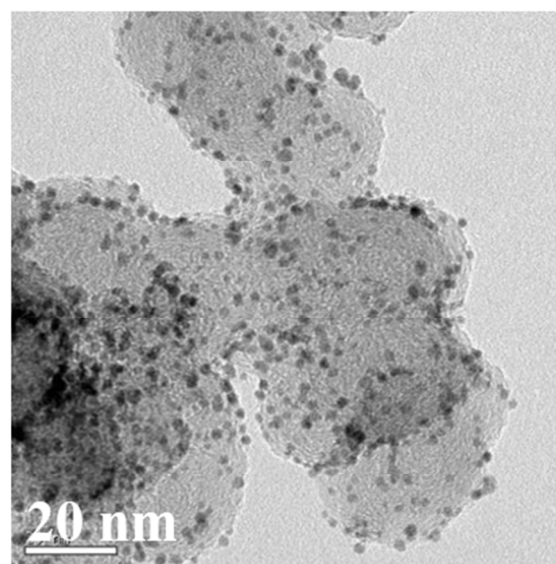


Fig. 4. TEM image of Pt-Ni-Cr (67:23:10)/C, and particle-size histogram.

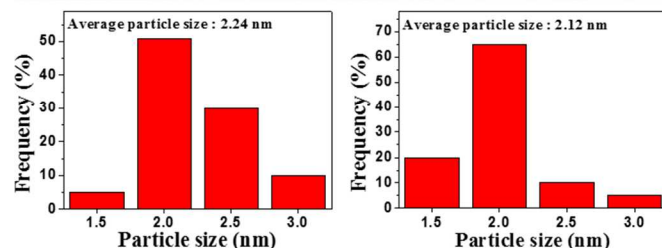
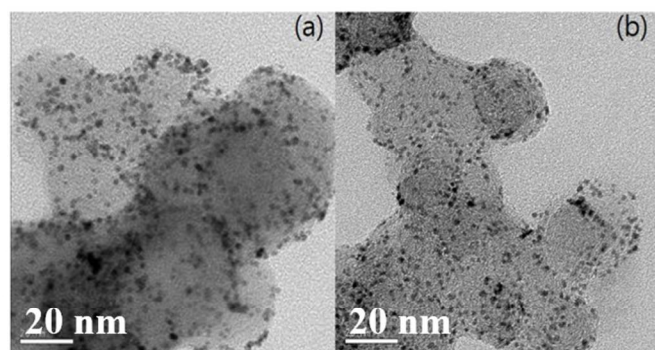


Fig. 3. TEM images of (a) Pt-Co-Cr (67:23:10)/C and (b) Pt-Co-Cr (45:45:10)/C, and particle-size histograms.

3.2. Electrochemical properties

The performances of a unit cell with a Pt-TM-Cr/C electrocatalyst and Pt-TM/C and Pt/C (E-TEK) electrocatalyst are compared in Figs. 5. The performances were measured at 80°C using H₂/O₂.²¹⁾ Fig. 5 shows that the nickel alloy catalyst performs worse than the Pt/C (E-TEK) catalyst. However, the Pt-Co-Cr/C catalyst performs better than the Pt-Ni-Cr/C catalyst with increasing Pt content, as shown in Fig. 5 (a). The Pt-Co-Cr (67:23:10)/C electrocatalyst showed a similar cell performance to that of the Pt/C electrocatalyst and better durability than the Pt-Co-Cr (45:45:10)/C electrocatalyst. According to the results, in Pt-Co-Cr

(45:45:10)/C, Co atoms were initially separated on the top of the electrocatalyst layer and likely to obstruct hydrogen adsorption onto the Pt atoms; this might be the cause of the relatively poor performance of Pt-Co-Cr (45:45:10)/C at low current densities. Pt-Co-Cr (45:45:10)/C catalysts have lower solubility of Co than Pt-Co-Cr (67:23:10)/C catalysts. Therefore, surplus Co is generated in Pt-Co-Cr (45:45:10)/C catalysts and impairs the reaction of the electrode, which reduces the performance and the speed of stabilization of the Pt-Co-Cr (45:45:10)/C catalyst. The degradation ratio of the Pt catalyst increased more than that of the other catalysts after 100 h operation time, as shown in fig. 5 (b). This result indicate that Cr added catalysts improve the electrode's durability.

The Pt-Co-Cr (67:23:10)/C showed compatible performance to the Pt/C cathode. After 100 h of operation, performance for Pt-Co-Cr (45:45:10) Pt-Co-Cr and Pt/C. The observed decay in cathodic performance Pt/C and Pt alloy/C could be explained by the dissolution of the alloying element for the Pt alloy and particle migration for the pure Pt/C. Similar results are reported in the literature Pt group metal and Pt alloy[28]. Pt/Cr alloy did not show any appeared leaching but showed leaching of the Pt/Ni alloy[29]. This study showed that the amount of transition metal and metal combination in the catalyst might be one of the factors in determining the performance of the catalyst. Further work is necessary to understand the effect of synthetic the different transition metal combination on the durability of the cathodic performance.”

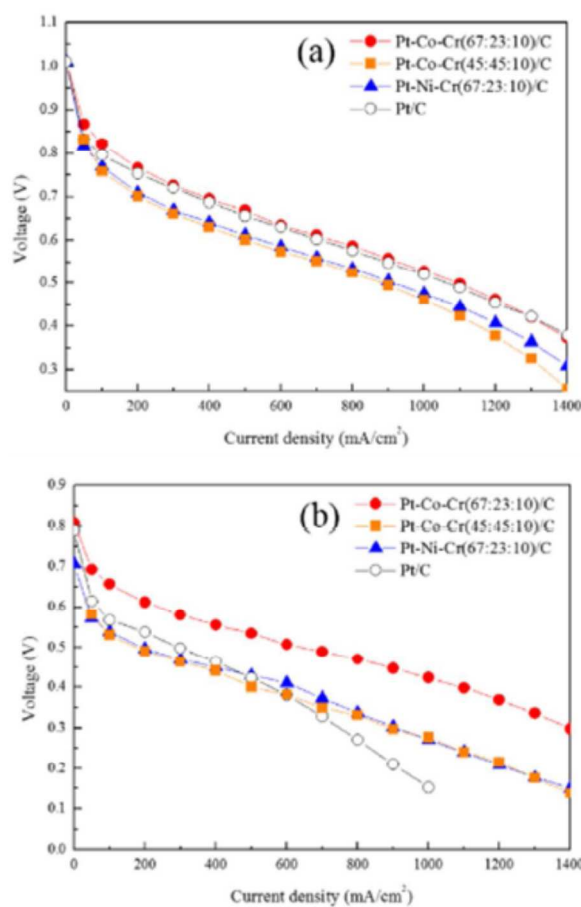


Fig. 5. Unit-cell performance of Pt-Co-Cr/C with different composition, Pt-Ni-Cr (67:23:10)/C and Pt electrocatalysts in initial state (a) and after 100 h operating (b). Fuel cell operation conditions; T cell: 80 °C, anode: H₂, cathode:

3.3. Stability test

Stability testing was performed for 100 h of cell operation. Each cathode was coated with four different catalysts, which were Pt/C, Pt-Co-Cr (67:23:10)/C, Pt-Co-Cr (45:45:10)/C, and Pt-Ni-Cr (67:23:10)/C. During the stability tests, the voltage was maintained at 0.6 V and the unit cells were kept at the temperature of 90°C. As shown in Fig. 6, the current for the Pt-Co-Cr (67:23:10)/C, Pt-Co-Cr (45:45:10)/C, and Pt-Ni-Cr (67:23:10)/C catalysts stabilized after 50, 70, and 90 h of cell test operation, respectively. Therefore, the time required to stabilize the Pt-Co-Cr (67:23:10)/C catalyst was 40 h less than that for the Pt-Ni-Cr (45:45:10)/C catalyst. During the initial stage of the stability test (i.e., <10 h), the cell performance of the Pt-Co-Cr (67:23:10)/C catalyst was better than those of the other catalysts, as shown in Fig. 6.

The degradation of the three catalysts was very similar over the following 30 h. The degradation ratio of the Pt-Co-Cr (67:23:10)/C catalyst reduced after 40 h and stabilized after 50 h. Stabilization of the Pt-Co-Cr (45:45:10)/C catalyst occurred after 70 h even though its speed of stabilization was slower than that of the Pt-Co-Cr (67:23:10)/C catalyst.

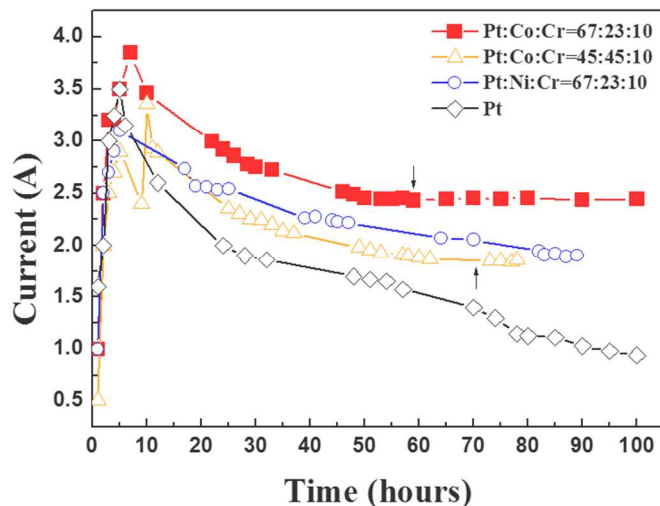


Fig. 6. Accelerated stability test results with different catalysts. Fuel cell operation conditions; T cell: 90°C, anode: H₂, cathode: O₂, Voltage: 0.6V.

It has been reported that addition of transition metals such as Co, Cr, Ni, Fe, etc enhances the electrocatalytic activity for ORR [22]. The enhancement of ORR activity for Pt alloy has been explained by geometric and electronic effect. Norskov et al also shows that higher catalytic activity can be achieved for Pt alloy due to the smaller binding energies [30]. However, the problem of stability of these materials have been reported[21]. Leaching or dissolution of the metal from Pt alloy are major causes for catalyst stability. The stability of Pt alloy varies with base metal. Pt alloyed with Cr showed more stable performance than the Fe and Ni probably due to forming stronger Pt-Cr bond and resulting higher stability in acid medium [29]

3.4. Stability degradation analysis

The cell performance of Pt/C (E-TEK) was degraded continuously even after 80 h, as shown in Fig. 7. Fig. 7(a) shows a TEM image of the Pt/C (E-TEK) catalyst after 100 h of the accelerated stability test. From the figure, it is evident that Pt particles agglomerated and grew to ~10 nm in

diameter. Because the large Pt particles are not efficient catalysts for the electrode reaction, unalloyed Pt particles were easily dissolved into the cell and the resultant dissolved Pt ions would joined with other Pt particles. Therefore, the Pt particles grow as evident in Fig. 7(a), and the cell performance is degraded as shown in Fig. 2. In contrast, the Pt-Co-Cr (67:23:10)/C catalyst did not undergo the similar increase of particle size and dissolution rate, which is demonstrated in Fig. 7(b). These results indicate that Cr, which is resistant to acid, formed an alloy with Pt:Co (3:1) thereby limiting catalyst dissolution. The reason can be found in the lattice parameter of catalysts. The lattice parameter of Pt-Co-Cr (67:23:10) is 0.3817 nm, while the lattice parameter of Pt catalyst is 0.3923 nm in compliance with Fig. 3. The dissolution energy of catalysts was increased as the lattice parameter became smaller. Accordingly, Pt-Co-Cr (67:23:10)/C catalysts perform better than the other catalysts and improve the durability of the electrode.

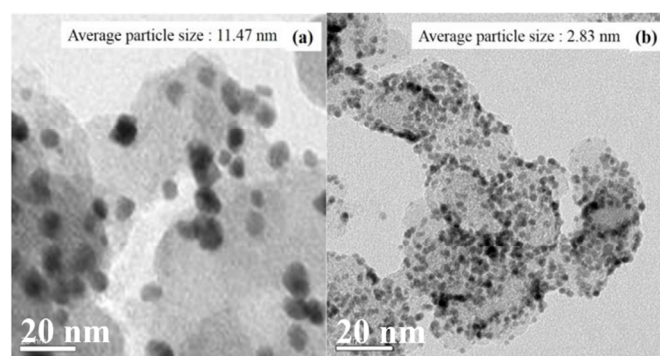


Fig. 7. TEM images of (a) Pt/C and (b) Pt-Co-Cr (67:23:10)/C after 100 h of durability testing.

4. Conclusions

Pt-TM-Cr/C alloy electrocatalysts were prepared using a polyol method. XRD, TEM, and ICP-AES analyses revealed the particle sizes, distribution properties, and compositions of the electrocatalysts. The electrocatalytic properties were investigated using unit-cell and stability tests. From the TEM images and XRD data, it is evident that the catalyst particles were distributed uniformly on the carbon (Vulcan XC-72) and the particle sizes were 2 ~ 5 nm, which is adequate for electrocatalysts. The electrode tests showed that the addition of Cr to the ternary electrocatalysts enhanced the durability of the electrodes in PEMFCs. Despite a reduction in the Pt loading, the unit-cell performance of the Pt-Co-Cr

(67:23:10)/C catalyst was similar to that of a commercial electrocatalysts (Pt/C (E-TEK)). The accelerated stability test showed that Cr prevents dissolution of the transition metal and improves the durability of the electrode.

Notes and references

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