Short communication

Using Pt sols to prepare low Pt-loading electrodes for polymer electrolyte fuel cells

Maksudur R. Khan [a,b,1], Shawn D. Lin [a,b,*]

[a] *The Fuel Cell Center, Yuan Ze University, Chung-Li, Taiwan 320, ROC*
[b] *Department of Chemical Engineering and Material Science, Yuan Ze University, Chung-Li, Taiwan 320, ROC*

Abstract

Novel platinum electrodes with controllable platinum loadings are prepared by direct deposition of platinum sols prepared with citrate and methanol. No extra treatment is needed except the evaporation of solvent. The platinum particles maintain a size similar to that of the original sols, as indicated by XRD data. The platinum-deposited membrane shows high specific activity and comparable single-cell performance with electrodes prepared from Pt/C catalysts. This electrode preparation method has the advantages of easy preparation and a good control for lowering the platinum-loading.
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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have emerged as candidates for transportation, portable and stationary power systems due to their good energy conversion efficiency and potentially high power density [1,2]. To make PEFCs a commercial reality, much development work is focusing on improving polymer electrolytes, electrocatalysts and electrode materials [3,4]. In particular, cost is a very important issue. The material cost of the polymer electrolyte membrane can be reduced either by a growth in the market size and/or by the use of less expensive non-fluoro polymers. The other key to reducing the material cost of PEFCs is to decrease the amount of Pt without sacrificing performance. This can be achieved by maximizing the utilization of Pt catalysts via optimizing the three-phase interface at every Pt active site in the electrodes [5]. A major progress in enhancing performance and reducing Pt loading has been achieved during the past few decades by using Pt/C instead of Pt black as the electrocatalyst, and by impregnation of a proton conductor (Nafion) into the catalyst layer of the gas-diffusion electrode [6–9]. Nevertheless, the Pt loading and its material cost are still too high for practical use. Catalyst sites not in direct contact with both the ionomer and the electron collector are non-reacting and cause poor Pt utilization [10]. Methods like tuning the Nafion loading in the catalyst layer [11,12] have been proposed to promote the interfacial contact between Pt particles and ionomers in order to boost utilization. Another approach tries to deposit Pt on the Nafion surface. Such preparation by a chemical reduction route [13,14] results, however, in poor catalyst utilization due to platinization of the membrane channels. O'Hayre et al. [15] deposited Pt on to a Nafion117 membrane by sputtering and a loading of $0.04\,\mathrm{mg\,Pt\,cm^{-2}}$ was found to given a performance comparable with a commercial MEA with a $0.4\,\mathrm{mg\,Pt\,cm^{-2}}$ loading. The disadvantages of this sputtering method are that the procedure is tedious and that the performance of the fuel cell changes dramatically with Pt loading.

Pt nanoparticles of controlled size and shape can be prepared by wet-chemistry methods among which the sol–gel method is widely practiced in the presence of stabilizers [16–21]. The use of such Pt nanoparticles for PEFCs has not been extensively investigated. The presence of a polymer stabilizer of high molecular weight is likely to be detrimental to the catalytic properties of Pt nanoparticles and is therefore undesirable. The removal of polymer stabilizing agents require oxidation or

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* Corresponding author. Tel.: +886 3 4638800x2554; fax: +886 3 4559373.
E-mail address: sdlin@saturn.yzu.edu.tw (S.D. Lin).
[1] Current address: Department of Chemical Engineering and Polymer Science, Shah Jalal University of Science and Technology, Sylhet 3114, Bangladesh.

decomposition at high temperatures which may result in particle sintering. We recently reported a sol–gel preparation method for Pt nanoparticles using a highly water-soluble lower molecular weight stabilizer, e.g., sodium citrate [22]. In the present work, we report the performance of electrodes prepared by depositing such prepared Pt nanoparticles on to a polymer electrolyte membrane. To show the advantage of using a stabilizer of lower molecular weight, the as-deposited electrodes are tested without extra pretreatment. The potential of using this method to prepare electrodes with ultra-low Pt loadings is indicated.

2. Experimental

2.1. Pt sols preparation

Pt nanoparticles with an average size of 2–3 nm were prepared by the method described elsewhere [22]. In brief, a mixture of 0.1 M $H_2PtCl_{6(aq)}$ and 0.1 M sodium citrate (J.T. Baker, 99.9%) was added to a methanol solution under reflux and stirring at 353 K. The reaction was stopped by quenching to room temperature immediately the solution turned black.

2.2. Electrode preparation

The prepared Pt sols were dispersed evenly on a Nafion 117 membrane (DuPont), and then the solvent was evaporated at room temperature. The loading was controlled by the amount of sol added for deposition. Prior to the deposition, membranes were boiled in deionized water for 30 min, followed by boiling in 1 M H_2SO_4 solution for 20 min, then copious washing with in deionized water at ∼80 °C. Pretreated membranes were stored in deionized water at room temperature. The prepared Pt/Nafion electrode can, if desired, be immersed in water at ∼60 °C for the removal of impurities and after that it was dried under vacuum at room temperature. In most cases, the Pt/Nafion electrode was used without washing.
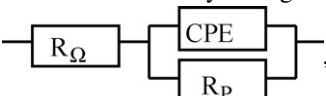
2.3. MEA preparation

The Pt/Nafion electrode was hot pressed with an electron conducting gas-diffusion layer (GDL), e.g., carbon paper (Torray) or carbon-coated carbon paper (SGL Carbon, Sigracet GDL10BB). The press temperature was varied from 30 to 110 °C and the press pressure was varied from 15 to 100 kg$_f$ cm^{-2}.

2.4. Electrochemical characterization

Pt/Nafion electrodes were evaluated in three ways: (i) active surface-area measurements by cyclic voltammetry (CV); (ii) polarization curves for the hydrogen oxidation (HOR) and oxygen reduction reactions (ORR); (iii) electrochemical impedance spectroscopy (EIS), with a potentiostat (Solatron 1287) and a frequency response analyzer (Solatron 1255B). For CV and half-cell polarization measurements, a single-side coated membrane of 2.5 cm^2 geometric electrode area was used. The electrode side was exposed to N_2 and the opposite face (membrane side) to 1 M H_2SO_4 solution. A platinum foil with a large area was used as

the counter electrode and an Ag/AgCl electrode, connected via a Luggin capillary, served as the reference. The reported potential is corrected to that versus RHE (reversible hydrogen electrode). The CV scan rate was 0.1 V s^{-1} over a potential range from 0 to 1.4 V (RHE) at 25 °C. The Pt active surface-area was estimated by integrating the charge of the hydrogen desorption region in the cyclic voltammogram, with double-layer charge correction and a conversion factor of 210 μC cm^{-2} Pt.

The same cell was used to obtain the hydrogen oxidation and oxygen reduction half-cell polarization curves. In these measurements, the electrode was exposed to either H_2 or O_2 at a flow rate of 70 cc min^{-1} using either galvanodynamic or potentiodynamic control. Half-cell EIS measurements were carried out at various cathodic potentials in the range of 0.55–0.8 V (RHE). An alternating sinusoidal signal of 10 mV peak-to-peak was superimposed on the d.c.-potential. The impedance spectrum was collected for frequencies between 20 kHz and 50 MHz. The polarization resistance was extracted by fitting EIS data with an equivalent circuit, , where R_Ω is the sum of electrode and electrolyte ohmic resistance, R_p the polarization resistance, and CPE is the constant phase element.

2.5. Single-cell study

Pt sols and a commercial 20 wt.% Pt/C (E-Tek) were used to coat either side of Nafion 117 membrane at the same Pt loading of 0.06 mg Pt/cm^2 with a Pt/Nafion of 1/11 (wt.) in all inks. No impurity removal procedure was adopted in this MEA preparation. The dry Pt-coated-membrane was hot-pressed with GDL at 110 °C and 15 kg$_f$ cm^{-2} for 90 s. For comparison, a MEA with a both-side coating of commercial 20 wt.% Pt/C was prepared similarly. A home-made 2 cm × 2 cm single cell was used to test the prepared MEA. Prior to I–V performance evaluation, the MEA was activated at 70/80/80 °C (cell/anode humidifier/cathode humidifier) and a back-pressure of 20 psi [23]. The current–potential (I–V) performance was evaluated by means of a potentiodynamic scan at 30/35/35 °C (cell/anode humidifier/cathode humidifier) and a flow rate of 50 cc min^{-1} of H_2 and O_2 at the anode and cathode, respectively. No back-pressure was applied unless otherwise specified.

2.6. XRD analysis

The prepared electrodes were mounted on glass plates using double-side tape. X-ray diffraction was undertaken with a commercial diffractometer (Shimadzu, XRD-6000) using Cu K$_\alpha$ radiation of 40 kV and 30 mA. Step scans were conducted between 30° and 60° (2θ) using a 0.5° step size and a 2.4 s dwell time. Apparent crystallite sizes were determined from the Pt (1 1 1) peak width (after subtraction of the Nafion background and correction for instrumental broadening) using the Scherrer Equation.
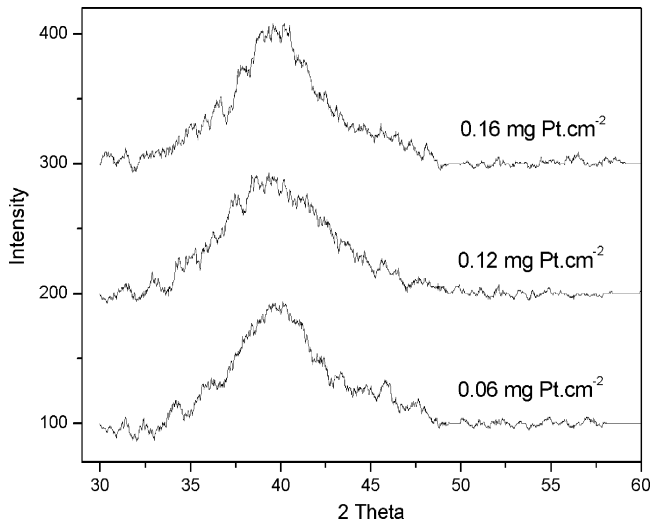
Fig. 1. X-ray diffraction spectra of as-prepared Pt-deposited Nafion 117 membranes at different Pt loadings. Diffraction peak is obtained after subtraction of Nafion diffraction background.

3. Results and discussion

### 3.1. Physical characterization by XRD

The as-prepared Pt-deposited Nafion 117 membranes from Pt sols were examined by X-ray diffraction. The data presented in Fig. 1 provide an estimated Pt particle size of about 2 nm with different Pt loadings as based on the diffraction peak broadening after the subtraction of the Nafion background. The average Pt size is close to that of the Pt sols [22], and this indicates that the deposition procedure does not influence the Pt particle size.

3.2. Half-cell HOR performance of Pt/Nafion electrodes

One-side Pt-coated membranes at various Pt loadings were placed, without pressing, with the Pt-side in contact with carbon paper (Torray) or carbon-coated carbon paper (SGL). Cyclic voltammograms for the HOR of such electrodes are given in Fig. 2. Limiting current density, specific area and activity are presented in Table 1. In comparison with higher-Pt-loaded elec-
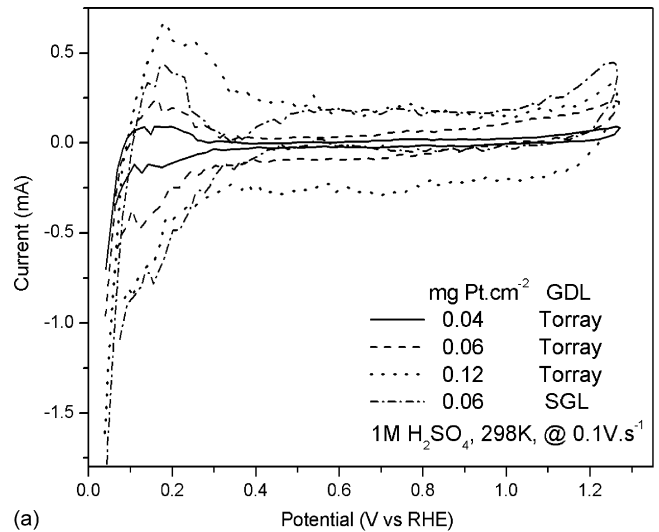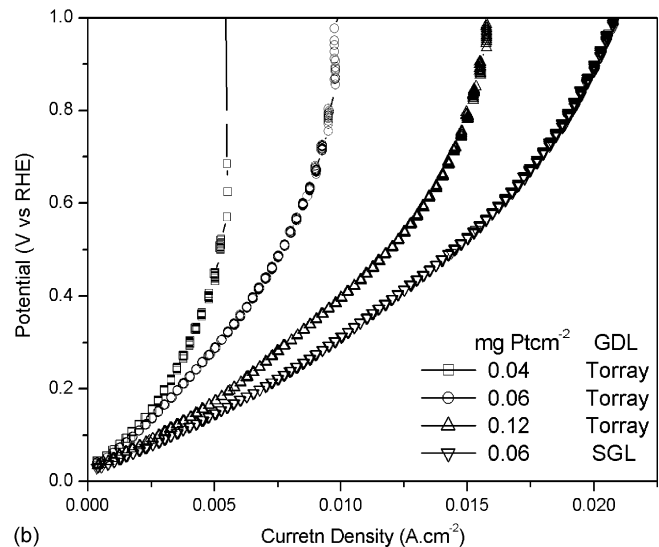
Fig. 2. (a) Cyclic voltammograms and (b) HOR polarization curves of Pt-deposited Nafion electrodes without hot-pressing on to GDL (galvanodynamic control, scan rate = 1 mV s^{-1}).

Table 1
Electrochemical activity[a] of HOR over Pt/Nafion electrodes

Loading (mg Pt cm^{-2})	Active area (cm^2 Pt)	I_{limit} (mA cm^{-2})	Specific area (m^2 Pt g^{-1} Pt)	Activity	
				mA cm^{-2} Pt	mA mg^{-1} Pt
0.04[b]	1.43	5.6	1.78	7.71	138
0.06[b]	2.86	10.0	2.38	7.02	167
0.12[b]	3.57	16.4	2.97	4.59	137
0.06[c]	4.76	22.3	3.97	9.36	371
0.55 [14]	118.9	440	34	2.35	800
3.6 [14]	297.5	580	13	1.23	160
4.1 [13]	182.5	450	7	1.57	110

[a] Activity is based on HOR limiting current from Pt/Nafion electrodes placed on GDL (no pressing) at 298 K, 1 M H$_2$SO$_4$.

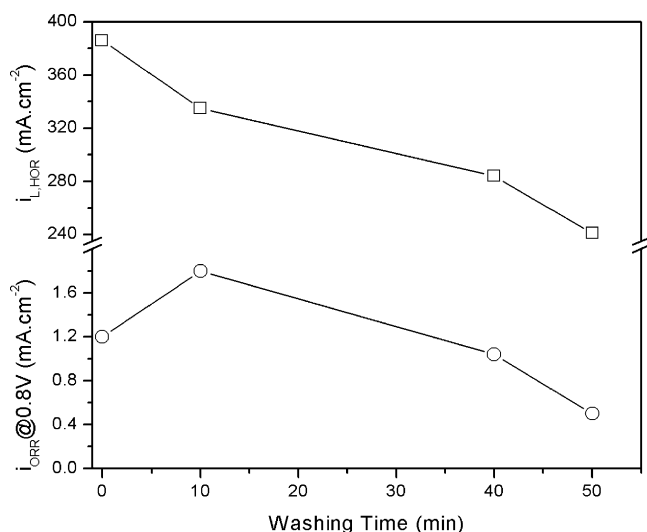[b] GDL: Toray carbon paper.

[c] GDL: SGL, coated carbon paper.

Fig. 3. HOR limiting current density and ORR current density at 0.8 V (vs. RHE) as function of washing time of Pt-deposited Nafion electrodes. Data shown at $t = 0$ min represent unwashed sample.
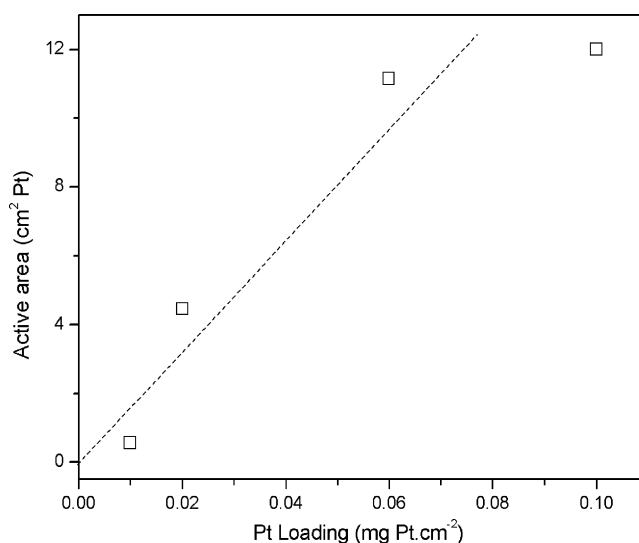

Fig. 4. Effect of Pt loading on measured Pt active area of Pt-deposited Nafion electrodes based on cyclic voltammograms. Pt/Nafion electrodes hot-pressed with carbon-coated carbon paper (SGL) at $110\,°C$ and $15\,kg_f\,cm^{-2}$ for 90 s.

trodes made by a chemical route [14], these results represent poor performances in all aspects except for the specific catalyst activity. The poor active area and limiting current density can be attributed to the poor current-collection efficiency because no pressing between the electrode and the GDL was conducted. This also indicates that the deposited Pt particles are isolated and not forming a continuous film. Using a smoother GDL (SGL paper with a carbon coating) as the current-collector results in about twice the hydrogen oxidation limiting current density and mass activity than when using a less-smooth GDL (Toray). This can be explained by the fact that the smoother GDL makes better contact with the distributed Pt particles. The prepared Pt/Nafion electrodes have a high specific activity although the current-collection efficiency is not good. This suggests that a significant boost in performance can be achieved if the catalyst layer has good contact with the electron-conducting GDL. Experimental data confirm that the pressed electrodes show a mass activity for HOR that is almost 30 times higher than that for unpressed counterparts.

3.3. Effect of sol impurities

The Pt-coated membranes described above were used as prepared. In order to know whether detrimental effects from either ingredients or by-products within the prepared sols would occur, some Pt/Nafion electrodes were pretreated by 'washing' in hot water (at $60\,°C$) prior to pressing against carbon-coated GDLs at $110\,°C$ and $15\,kg_f\,cm^{-2}$ for 90 s. The half-cell performance of the washed electrodes is presented in Fig. 3. For the anode, a monotonic decrease in the limiting current density can be observed with increasing washing time. The loss of Pt from the surface through leaching might be the reason for the decline in anode performance. The unwashed electrodes are expected to contain citrate, Na^+ and Cl^-, but still give the maximum performance as an anode. This suggests that these ingredients in the prepared Pt sols do not suppress the catalytic activity of

Pt/Nafion for HOR. On the other hand, the cathode mass activity at 0.8 V increases after a 15 min washing in spite of the Pt loss. EIS analysis shows that the polarization resistance of the ORR at 0.8 V decreases after a 15 min washing. This suggests that ORR activity is affected by the presence of these ingredients from the Pt sols preparation. A further drop in cathode performance after prolonged washing can be attributed to excess loss of Pt. These results indicate that the anode preparation procedures can be made very simple using the Pt sols in this study; whereas a certain washing procedure may be needed for optimum cathode performance.

3.4. Effect of Pt loading

The measured Pt active area of the prepared Pt/Nafion electrodes as a function of Pt loading is shown in Fig. 4. No washing of the prepared electrodes was performed. The Pt loading was varied from 0.01 to 0.1 mg cm^{-2} by dispersing different amounts of sol during electrode preparation. The active area increases almost linearly as the loading increases and this indicates no change in Pt sols at loadings within the test range. The influence of Pt loading on HOR and ORR mass activity is shown in Fig. 5 for electrodes prepared at pressing conditions of $110\,°C$ and $100\,kg_f\,cm^{-2}$ for 90 s. For the HOR, a maximum mass activity is observed at a 0.02 mg Pt cm^{-2} loading. The mass activity of ORR at 0.8 V (versus RHE) appears to have a maximum at a loading of about 0.03 mg Pt cm^{-2}, but the trend is not as obvious as that for the HOR. The maximum anode and cathode mass activity in Fig. 5 are comparable with the best performance reported for anodes [24] and cathodes [11].

3.5. Single-cell study

Now the question arises whether this method of MEA preparation is applicable for a single cell. The iR-corrected polarization curves and the EIS data at 0.8 V for MEAs with Pt sols
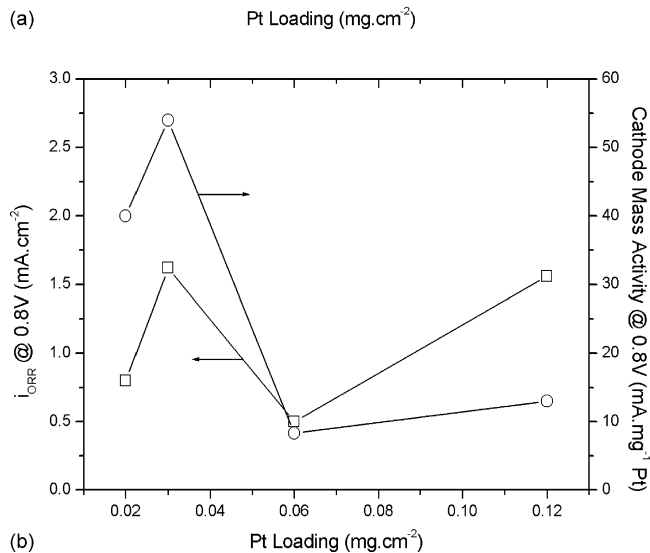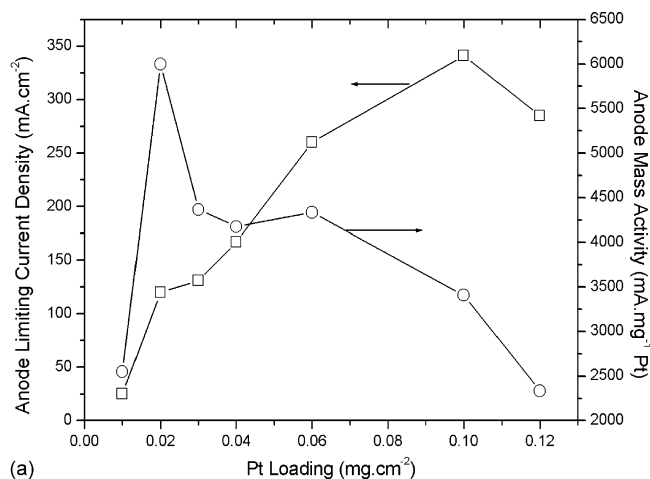
Fig. 5. Effect of Pt loading on half-cell (a) HOR and (b) ORR performance of Pt-deposited Nafion electrodes.

Fig. 6. Single-cell (a) polarization curves after iR correction and (b) Niquist plot based on a.c. impedance spectroscopy at 0.8 V (vs. RHE) for differently prepared MEAs. All electrodes have 0.06 mg Pt cm^{-2} loading. Single-cell test conditions: 30/35/35 °C (cell/anode humidifier/cathode humidifier) and a flow rate of 50 cc min^{-1} of H$_2$ and O$_2$ at both anode and cathode; no back-pressure applied unless otherwise specified.

cathodes or anodes are presented in Fig. 6. A comparison is made to the performance of MEAs prepared with a commercial Pt/C catalyst as the cathode or the anode. A Pt sol anode in conjunction with a commercial Pt/C cathode results in a I–V performance similar to that using the commercial Pt/C electrode on both sides. This is consistent with the understanding that the cathode dominates single-cell performance. Although the I–V performance is significantly lower when Pt sols are used as the cathode, a small back-pressure of 10 psi at cathode boosts the performance dramatically. This suggests that the electrochemical performance of a Pt sols electrode can be optimized via tuning of the cell operating parameters. The Pt sols are thus confirmed capable of preparing low-Pt-loading electrodes without sacrificing performance.

The a.c. impedance spectra for the above MEAs at 0.8 V with the fitted model parameters is given in Fig. 6(b). When a Pt sol cathode is used without back-pressure, a very high polarization resistance is found, but this drops drastically with 10 psi of back-pressure. One possible explanation is that the back-pressure changes the interfacial contact of deposited Pt, probably by alteration of the water film over the Pt sites. Impedance data-fitting also demonstrates a slight decrease in ohmic resistance
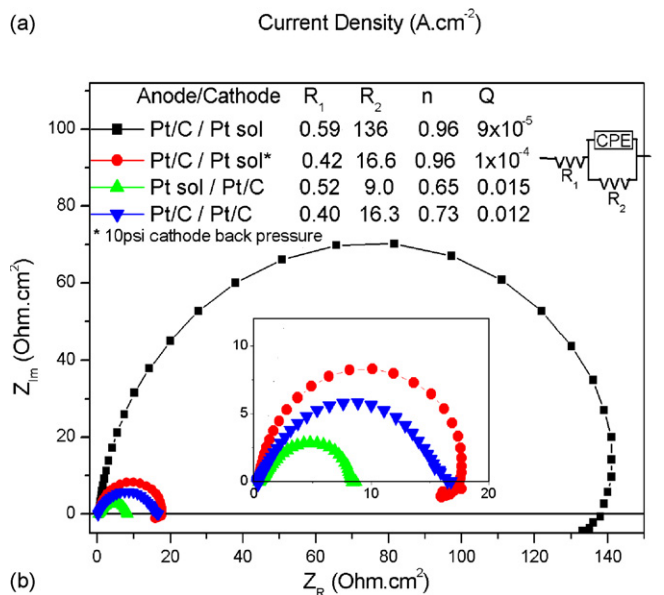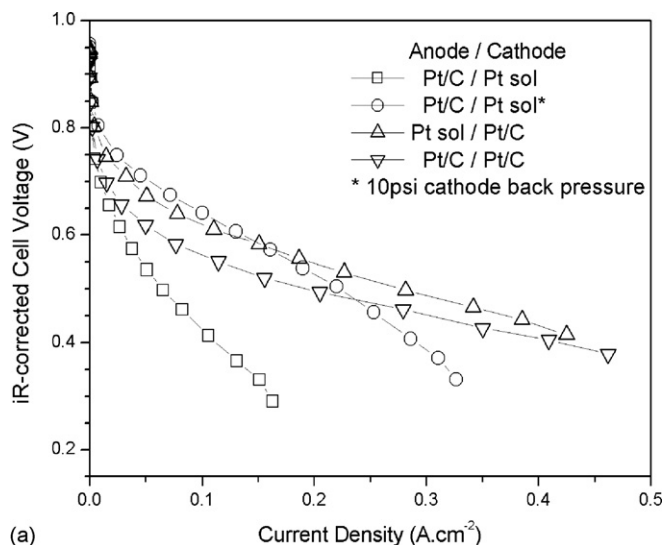
(from 0.59 to 0.42 Ω cm^2) by the application of 10 psi back-pressure. This suggests that an increased proton conductivity results from the back-pressure. Another important feature of the Pt sols electrodes in comparison with the MEA prepared with Pt/C is the shape of the impedance plot. A suppressed arc in the Niquist plot of Pt/C coated MEA indicates that the catalyst layer has an inhomogeneous or a rough surface [25], whereas the Pt sols-coated MEA appears to have a more homogeneous electrode surface as demonstrated by a fitting value of n very close to 1.

Single-cell studies reveal that the present method of MEA preparation has certain advantages over conventional methods using Pt/C catalysts. First, the Pt sol-prepared MEAs have performances comparable with those prepared with Pt/C catalysts. Second, the Pt loading can be easily lowered by about an order

of magnitude by using the Pt sols. Third, the procedure of this electrode preparation can be very simple. The power output of a single cell with a Pt sol-cathode (0.06 mg Pt cm^{-2}, 300 K, 10 psi back-pressure) is around 10 mW cm^{-2}. The maximum power from a Pt-sputtered-MEA (about 0.04 mg Pt cm^{-2}) is ca. 20 mW cm^{-2} (at 300 K, O$_2$, no back-pressure) [15]. This is better than the electrode performance found here but the sputtering techniques require expensive instruments and complex procedures. Furthermore, the performance of the Pt-sputtered-MEA is very sensitive to Pt loading [15] whereas the Pt sol-MEA is not. The Pt sol-prepared electrodes can be used without any pretreatment, even though EDX of the prepared MEA shows the presence of traces of Cl. It is therefore considered that this MEA preparation method from Pt sols will provide an avenue to low-Pt-loading electrodes and that further improvement will be realized.

4. Conclusion

A Pt electrode preparation method has been developed by immobilizing the Pt nanoparticles from Pt sols onto a Nafion membrane. The Pt loading can be controlled by varying the sol amount and can be as low as 0.01 mg cm^{-2}. X-ray diffraction and electrochemical active area analyses reveal no change in Pt particle size during deposition. The impurities present in the prepared sols do not diminish anode performance, whereas the cathode performance appears to be slightly hindered. Both half-cell mass activity and single-cell performance demonstrated the applicability of such electrodes. Preliminary results indicate that cathode performance can be further improved by either tuning the operating conditions or removing impurities.

Acknowledgements

References

[1] S. Srinivasan, J. Electrochem. Soc. 136 (1989) 41C.
[2] S. Gottesfeld, T.A. Zawodzinski, in: R.C. Alkire, H. Gerischer, D.M. Kolb, C.W. Tobias (Eds.), Advances in Electrochemical Science and Engineering, vol. 5, Wiley, Weinheim, 1997, pp. 195–301.
[3] K.B. Prater, J. Power Sources 51 (1994) 129.
[4] K. Kordesch, G. Simander, Fuel Cells and their Applications, VCH, Germany, 1996, p. 73.
[5] E. Middelman, Fuel Cell Bull. (2002) 9.
[6] S. Srinivasan, E.A. Ticianelli, C.R. Derouin, A. Redondo, J. Power Sources 22 (1988) 359.
[7] I.D. Raistrick, US Patent No. 4,876,115 (1989).
[8] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
[9] G.S. Kumar, M. Raja, S. Parthasarathy, Electrochim. Acta 40 (1995) 285.
[10] M.K. Debe, R.J. Poirier, M.K. Wackerfuss, R.J. Zigler, US Patent No. 6,319,293 B1 (2001).
[11] M. Uchida, Y. Aoyama, N. Eda, A. Otha, J. Electrochem. Soc. 142 (1995) 4143.
[12] E. Antolini, L. Giorgi, A. Pozio, E. Passalacqua, J. Power Sources 77 (1999) 136.
[13] H. Takenaka, E. Torikai, Japan Patent No. 5538934 (1980).
[14] R. Liu, W.-H. Her, P.S. Fediw, J. Electrochem. Soc. 139 (1992) 15.
[15] R. O'Hayre, S.J. Lee, S.W. Cha, F.B. Prinz, J. Power Sources 109 (2002) 483.
[16] D.G. Duff, P.P. Edwards, B.F.G. Johnson, J. Phys. Chem. 99 (1995) 15934.
[17] C.-W. Chen, D. Tano, M. Akashi, J. Colloid Interface Sci. 225 (2000) 349.
[18] T. Teranishi, M. Hosoe, T. Tanaka, M. Miyake, J. Phys. Chem. B 103 (1999) 3818.
[19] D.N. Furlong, A. Launikonis, W.H.F. Sasse, J. Chem. Soc. Faraday Trans. I80 (1984) 571.
[20] C.-W. Chen, M. Akashi, Langmuir 13 (1997) 6465.
[21] K. Jüttner, K.-M. Mangold, M. Lange, K. Bouzek, Russ. J. Electrochem. 40 (2004) 317.
[22] C.-H. Lin, M.R. Khan, S.D. Lin, J. Colloid Interface Sci. 299 (2006) 678.
[23] Z. Qi, A. Kaufman, J. Power Sources 114 (2003) 21.
[24] A. Pozio, L. Giorgi, E. Antolini, E. Passalacqua, Electrochim. Acta 46 (2000) 555.
[25] C.-H. Kim, S.-I. Pyun, J.-H. Kim, Electrochim. Acta 48 (2003) 3455.