

FORMATION AND ELECTRO-CATALYTIC PERFORMANCE OF PLATINUM-ALLOY NANO-PARTICLES ON CARBON AS CATHODE CATALYSTS FOR DIRECT $\text{NaBH}_4\text{-H}_2\text{O}_2$ FUEL CELLS

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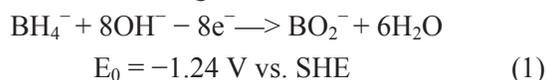
Abstract: The paper reports the preparation and characterization of Pt alloy nano-particles, which are directly reduced on carbon-black to serve as catalyst of direct $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel-cells. Two Pt/C nano-catalysts with different platinum content as well as Pt-Mn/C and Pt-Co/C nano-alloy catalysts are prepared using impregnation reduction method. The test results show that the average particle sizes of Pt-Mn/C and Pt-Co/C are smaller than the two pure Pt/C catalysts. Relative to the pure Pt/C catalysts, the two Pt alloy nano-catalysts feature lower lattice constants, smaller degree of crystallinity, higher reductive peak potentials, bigger peak currents and better stability.

Keywords: Pt alloy, cathode electro-catalyst, electrochemical reduction, $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel cell

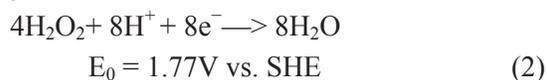
INTRODUCTION

Fuel cells have attracted attention for application in portable electronic devices because of their high fuel efficiency and non-pollution. With the rapid development of various fuel cell design, it is likely that, within the next two decades, power generation for portable electronic equipment and vehicular transportation will employ fuel cells as the power supply. H_2O_2 has lower activation energy, higher energy density and cheaper price than O_2 . Besides, it is easy to be transported and stored. All the above-mentioned advantages attract more and more researchers to develop fuel cells using H_2O_2 as the oxidant, such as direct $\text{NaBH}_4\text{-H}_2\text{O}_2$ fuel cell (DBHFC) and direct methanol- H_2O_2 fuel cell [1-5].

In DBHFC, sodium borohydride is oxidized at anode based on following reactions of



Hydrogen peroxide is restored at cathode according to following reactions of



Accordingly, the net cell reaction in DBHFC is



The theoretical fuel cell potential and specific energy of DBHFC are 3.01V and 17.06KWh/kg, respectively.

Normally, noble metals like Pt have been chosen as H_2O_2 catalysts due to the high catalytic activity and excellent stability [6-9]. For example, Choudhury et al. [9] used Pt/C as electro-reduction catalyst of H_2O_2 and AB_5 as electrochemical oxidation catalyst of NaBH_4 . Their battery was with the peak output power reaching $145\text{mW}\cdot\text{cm}^{-2}$ in aqueous alkaline. By now, however, few in-depth study has been focused on Pt-alloy catalysis for H_2O_2 . In this research, we use impregnation-chemical reduction method to prepared Pt-Co/C and Pt-Mn/C alloy-catalysts (metal content=10% in either case) and compare them with Pt₁/C (containing 10% Pt) and Pt₂/C (20% Pt). Reductive peak currents of the catalysts are tested to compare their electro-catalytic performance. The tested current-time curves are used to evaluate their stability. The chemical constructions of the catalysts are analyzed by XRD technique.

EXPERIMENTS

Preparation of electro-catalyst

90mg pretreated XC-72 carbon black is put in a 250mL beaker, with 70mL deionized water and 30mL isopropyl alcohol added. The mixer is ultrasound dispersed for 0.5h to form suspension. 1mL aqueous H_2PtCl_6 with 0.01g/mL platinum is slowly dipped into the scattered carbon suspension and, then, ultrasound dispersed for 1h. The PH value of the suspension is adjusted to weak alkali with NaOH solution. excessive $NaBH_4$ solution is gradually added and stirred for reaction, while the temperature is controlled at 80-90°C. The mixture is filtered in vacuum and washed with deionized water for three times. Finally, the filtered sample is moved into a constant temperature (80°C) vacuum drying oven for 24hrs. Finally we get the Pt_1/C catalyst with 10%Pt (weight percent). The catalysts of Pt_2/C (20% Pt), Pt-Co/C and Pt-Mn/C (metal content=10% in either case) are prepared in similar way.

Preparation of working electrode

The prepared 5mg catalyst is added with a small amount of 0.5% Nafion solution and, then, ultrasonic dispersed for a few minutes until an uniform ink-like sample is obtained. The catalyst ink is coated at one side of carbon paper and, then, put in a 40°C oven for 30min. The working electrode area is $0.5cm^2$ and the catalyst coating density is about $2mg/cm^2$.

Electrochemical test

Electrochemical performance test is conducted at 20°C, by using a CHI 660D electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd.). The working electrode is prepared as above mentioned. The reference electrode is saturated calomel electrode. The auxiliary electrode is a platinum foil with $2cm^2$ area. The electrolyte solution is the mixed solution of 0.5mol/L H_2SO_4 and 0.05mol/L H_2O_2 . Before test, nitrogen is introduced for 30min to remove the oxygen in the solution.

RESULTS AND DISCUSSION

XRD results in Fig. 1 show that the four catalysts are with face-centered cubic structures. It indicates that no change in basic crystal structure occurs due to the addition of Mn or Co into Pt, i.e., the Pt atoms in

the cell unit are replaced by Mn or Co. According to the results listed in Table 1, the two alloy catalysts are with the lattice constant decreased, compared with the Pt/C catalysts, thereby, significantly increasing the active site number in the catalysts.

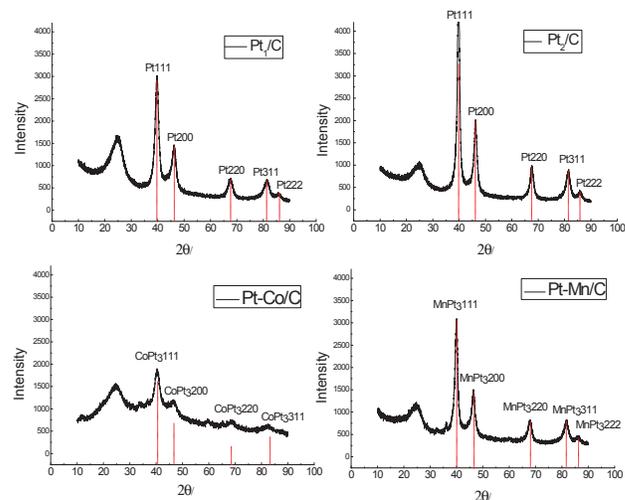


Fig. 1: XRD spectra of the four catalysts.

Calculated with Scherrer equation, the average dimensions of the 4 kinds of nano-particles (listed in Table 1) is consistent with the sizes measured in the TEM images of Fig. 2. By comparing the data of Pt_1/C with Pt_2/C in Table 1, the results indicate that increasing Pt content will enhance both the degree of crystallization and the catalyst particle size, which does not facilitate the electro-catalytic reaction. More importantly, it can be clearly seen that the average size of the alloy catalysts are obviously smaller than that of the Pt_2/C , thereby, being conducive to increase the specific surface-area for optimal catalysis.

Table 1. Average particle size and lattice constant of the four catalysts.

| Catalyst | Pt_1/C | Pt_2/C | Pt-Mn/C | Pt-Co/C |
|----------------------|----------|----------|---------|---------|
| grain size (nm) | 5.4 | 7.8 | 6.7 | 5.1 |
| lattice constant (Å) | 3.93 | 3.92 | 3.89 | 3.85 |

The electrochemical characterization is implemented sequentially with cyclic voltammetry, linear sweep voltammetry and current-time curve. The

measured cyclic voltammetry (CV) curves in Fig. 3 show that, addition of Mn or Co into the alloy has the same effect as increasing Pt of equal amount. Moreover, the catalytic ability of Pt-Co/C is even stronger than Pt₂/C. This phenomenon is helpful for saving noble metal resources. The linear sweep voltammetry curves shown in Fig. 4 further conform the CV curves. Both Pt-Co/C and Pt₂/C exhibit the highest reduction current in the *i-t* curves shown in Fig. 5. The reduction currents of Pt-Co/C and Pt-Mn/C show almost no attenuation throughout the reaction process, which indicates the better stability of the alloy catalysis compared to the non-alloy catalysts.

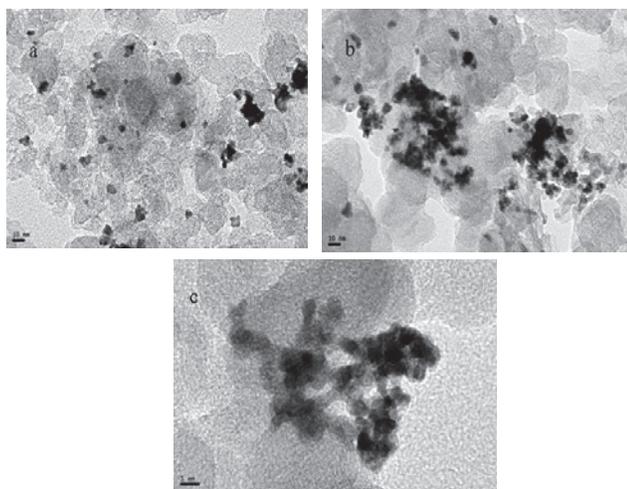


Fig. 2: TEM images of Pt₂/C (a), Pt-Mn/C (b) and Pt-Co/C (c).

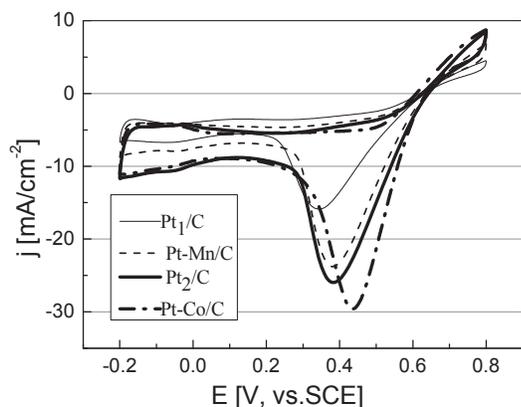


Fig. 3: Cyclic voltammetric curves of the 4 catalysts in H₂SO₄-H₂O₂ mixing solution.

With further optimal preparation of the Pt-alloy

catalyst for inhibition of possible coalescence of the particles, the Pt-alloy/C NPs are promising in fuel cell applications.

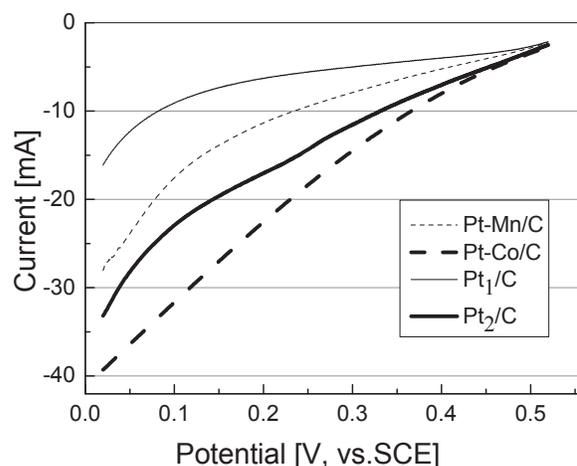


Fig. 4: Linear sweeping voltammetric curves of the 4 catalysts in H₂SO₄ + H₂O₂ solution.

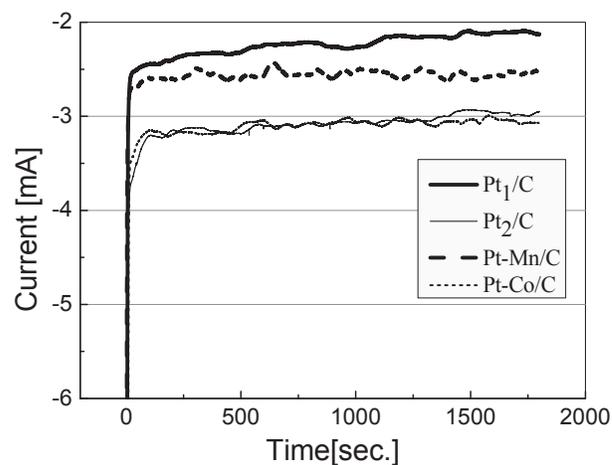


Fig. 5: Tested *i-t* curves of the 4 catalysts in H₂SO₄ + H₂O₂ solution.

CONCLUSION

Using impregnation-chemical reduction method, we prepare Pt₁/C, Pt₂/C, Pt-Co/C and Pt-Mn/C nano-catalysts. The XRD results indicate that all the 4 catalysts prepared by the impregnation-chemical reduction method are in face-centered cubic structure. The existence of Co and Mn are beneficial to reduce the crystallization degree of Pt-Co/C and Pt-Mn/C, thereby, increasing the active sites of the catalysts.

Such optimally designed catalysts are helpful for electrochemical reduction reaction. Compared to pure Pt/C, the Pt-Co/C and Pt-Mn/C show better catalytic stability and higher reductive peak current.

ACKNOWLEDGEMENTS

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