Oxygen Reduction Reaction Enhancement of PdCo/C Electrocatalysts Driven by Oxidation Treatment

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ABSTRACT

The effect of oxidation treatment induced progressive enhancement on oxygen reduction reaction (ORR) activities of PdCo/C catalysts is studied. Based on the XPS characterization, a new term, degree of surface oxidation (DSO), is proposed to illustrate their relationship between ORR activity and surface oxidation extent. It can be obviously found the optimal temperature for the promotion of ORR activity on various oxidized samples is 520 K. The improved ORR activity is ascribed to the formation of surface PdO species with 100 % DSO value.

Keywords: PdCo/C; oxidation treatment; degree of surface oxidation (DSO); oxygen reduction reaction (ORR); PdO.

1 INTRODUCTION

Carbon supported platinum (Pt/C) or other noble metals have been extensively used as cathode electrocatalysts for the oxygen reduction reaction (ORR) [1-3]. More recently, due to the rising price of Pt and the sluggish kinetics on ORR, the development of Pd-based or non-Pt bimetallic catalysts plays a decisive role in the wide-spread commercialization of this green technology [4-8]. Fernandez et al. [9] have demonstrated the main concept for choosing high performance Pd-M alloy catalysts based on the thermodynamic model. As illustrated, the main function of the incorporation of active elements (M) such as Co can facilitate the dissociation of O-O bond and thereby the produced Co-Oads species may transfer to the Pd site in which the electrochemical reduction reaction takes place immediately. Moreover, Suo et al. [10] have proposed the design consideration for the preparation of Pd-Co alloy catalysts. They have indicated that the alloying effect influences the lattice-strain and surface-ligand of the catalysts. As a result, Pd-Co bimetallic catalysts with the Pd shell/alloy core structure can display excellent ORR activity.

Besides, the post heat treatment may provide alternative ways to improve both the electro-catalytic activity and durability of the catalysts due to the enhancement of alloying extents, the removal of residual surfactants, the formation of some specific core-shell structures, and/or the alteration of the surface states [11-17]. In terms of the cathode catalysts, various approaches including heat treatment in oxidative, inert or reducing atmospheres have been applied on the Pt, Pt-based and Pd-based electrocatalysts to significantly promote the ORR activity [17-22]. Although the post-thermal treatment using either hydrogen or inert atmosphere on catalysts is commonly considered as an indispensible strategy for the promotion of their ORR activity, to the best of our knowledge, there is a paucity of reported studies on the oxidation–activity relationship of the catalysts. Herein, the main impetus of this study has highlighted the modification of Pd catalysts via the synergistic effect of Co alloying and oxidation treatment. For this purpose, the Pd-Co catalysts have been prepared via the deposition-precipitation (DP) route and various amounts of Pd surface oxides (Pd^sO) have been produced during the oxidation treatment process at 320-620 K. Their surface compositions, surface species, structures, particle sizes, and ORR performance can be explicitly elucidated.

2 EXPERIMENTAL SECTION

2.1 Preparation of catalysts

The PdCo/C alloy catalysts with Pd/Co atomic ratio of 3 to 1 and 20 % of metal loading were prepared by the deposition-precipitation (DP) method. Palladium nitrate and cobalt nitrate in the desired stoichiometry were co-deposited onto the commercial C black (Vulcan XC-72R) at 340 K by controlling the pH value to 9. The solution was stirred, subsequently filtered extensively with DI water, dried at 320 K for 24 h, reduced in an atmosphere of flowing H2/N2 (10/90 vol. %) gas at 390 K for 1 h and stored as fresh Pd_3Co_1/C catalysts. Afterwards, the oxidation treatment was performed in air at a temperature ranging from 320 - 620 K for 1 h. The catalysts after air heat treatments were referred to as OT (T = the oxidation temperature, 320-620 K).

2.2 Physical characterization of catalysts

The phase structures of various catalysts were accomplished by using Shimadzu X-ray diffractometer (XRD) with the CuKα radiation source operating at 40 kV and 25 mA. The morphologies for various oxidized samples were determined by transmission electron microscopy (TEM, JEOL-2100) equipped with a LaB_6 electron gun source and operated at 200 kV. An X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe) using an Al Kα radiation was used to study the surface compositions of the alloy catalysts.

2.3 Electrochemical measurements

Oxygen reduction current was measured via linear sweep voltammetry (LSV) method with a scan rate of 5 mVs^{-1} and a rotation speed of 1600 rpm in a single compartment three-electrode configuration. Rotating disk electrode (RDE) imbedded with a Teflon holder was used as the working electrode. During each measurement, a moderate O_2 gas flow was kept above the electrolyte. The current density at E = 0.7 V, I_{07}, within the mixed kinetic-diffusion region was used for comparison.

The stability of the catalysts was conducted via cyclic voltammograms (CV) characterization on an identical three electrode system as documented by Sarkar et al [23]. The CV plots were recorded at a scan rate of 20 mVs^{-1} in the N_2-saturated 0.1 M HClO4 aqueous solution between -0.24 and 1.1 V (vs. SCE). All potentials throughout this study are quoted with respect to the normal hydrogen electrode (NHE)..

3 RESULTS AND DISCUSSION

Fig. 1 displays the XRD patterns for the as-prepared and various oxidized PdCo/C catalysts. The vertical dot line represents the peak position of (111) diffraction for metallic Pd (JCPDS 46-1043). Noticeably, the peaks observed at around 40.6, 47.0, and 69.0^o are attributed to the reflections of Pd-Co alloys. While the oxidation temperature increases from 320 to 420 K, the diffraction peaks suggest no formation of oxide phases. However, on raising the temperature to 470 ~ 520 K, the reflections corresponding to metallic Pd-Co alloys vanish gradually and the characteristic peaks of PdO (JCPDS 02-1432) are apparently observed. Furthermore, the weak peak belonging to (200) diffraction of CoO (JCPDS 43-1004) phase is also found at 42.4^o. For O620 sample, the peak of C becomes insignificant, and peaks of metallic Pd, PdO, and CoO are apparently noted, indicating that the severe heat treatment results in C burning, sintering, oxidation, and phase separation of the alloy catalysts.

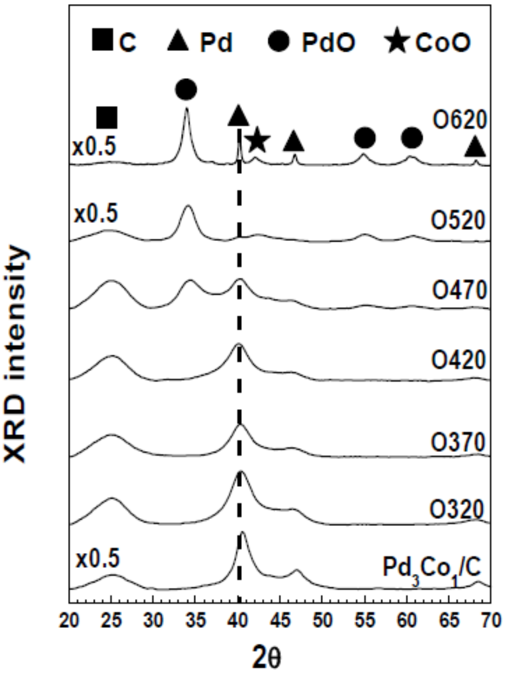

Figure 1: XRD patterns of the as-prepared and various oxidized PdCo/C catalysts. The vertical dot line represents the peak position of (111) diffraction for metallic Pd.

The morphologies and particle size distribution histograms of various PdCo/C catalysts based on the TEM

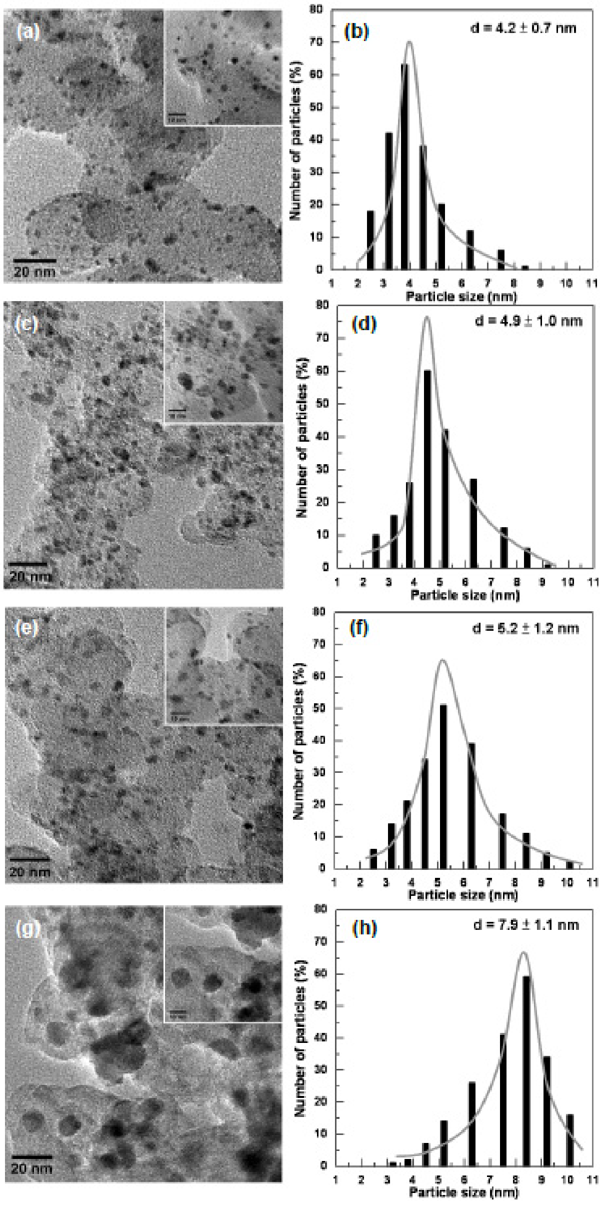

Figure 2 TEM micrographs and the corresponding particle size distribution histograms for the (a,b) as-prepared, (c,d) O420, (e,f) O520 and (g,h) O620 PdCo/C catalysts.

characterization are determined in Fig. 2. The Pd-Co NPs for as-prepared catalysts are uniformly dispersed on the C support with the mean particle size of around 4.2 ± 0.7 nm. Although high oxidation temperature is applied on the PdCo catalysts, however, the variation in particle size and dispersion is not significant, revealing that the temperature of 470 ~ 520 K is not sufficient for generation of severe sintering phenomenon of NPs (the particle size for O470 and O520 is 4.9 ± 1.0 nm and 5.2 ± 1.2 nm, respectively). In contrast, the severe post thermal treatment at 620 K contributes to the dramatic grain growth and sintering of NPs and the size is around 7.9 ± 1.1 nm.

The XPS spectra of Pd 3d for various oxidized Pd-Co catalysts are depicted and their experimental (black solid line) and fitting results (open circle line) of metallic and oxidized Pd are compared in Fig. 3. For the as-prepared sample, 30 at% of surface Pd exists as the oxide phase which is not observed in the XRD pattern, suggesting that those oxide phase may exist as amorphous state [24]. As increasing heating temperature, the metallic Pd phase gradually diminishes and the PdO phase dominates on the surface. When the oxidation temperature is higher than 520 K, it is unambiguous to note that surface Pd is fully oxidized and consequently only one set of PdO peaks is found. Hereafter, we define a new term, degree of surface oxidation (DSO), based on the percentage of surface PdO (denoted as Pd^{s}O) characterized by the peak fitting results of XPS spectra in order to thoroughly realize the correlation between surface oxide species and ORR activities. The DSO of as-prepared, O470, and O520 sample is 30, 81, 100 %, respectively.

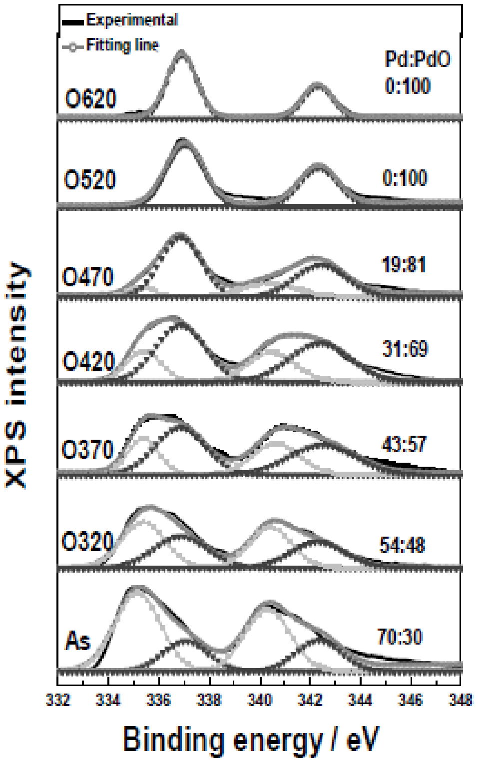

Figure 3: XPS spectra of Pd 3d for various PdCo/C catalysts. Their surface compositions of Pd and PdO are also compared.

The electro-catalytic activities for various oxidized Pd and Pd-Co catalysts are determined by LSV measurement. In order to scrutinize the ORR activity - DSO value relationship, the comparison is summarized in Fig. 4. It is manifestly observed that the ORR activity is correlated to the DSO value. The improvement of ORR activity reaches an optimal value ca. 2.3 mA cm^{-2} for the O520 sample where the complete formation of PdsO and the highest DSO value (100 %) is attained.

4 CONCLUSIONS

The effect of oxidation treatment on the improvement of ORR activity for the PdCo/C catalysts has been systematically investigated. By virtue of the XPS technique, an index, DSO has been defined to explicitly illustrate the relationship between electrochemical property and the oxidation temperature. From our observations, the catalytic-activity and durability of Pd catalysts can be well-promoted by oxidation treatment. The optimum oxidation condition for the enhancement of ORR performance is at 520 K, where the surface of catalysts is mainly covered by PdO and the DSO is 100 %.

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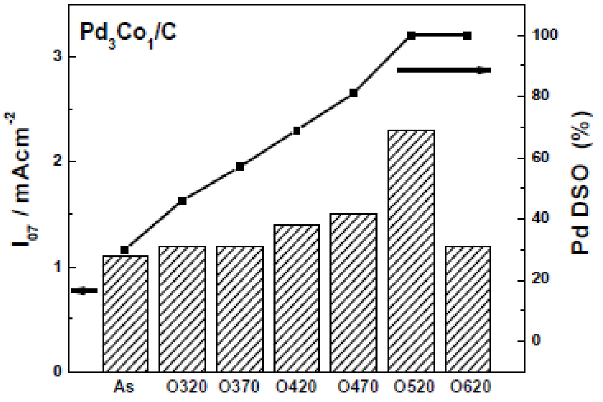

Figure 4 : The correlation of ORR activity and DSO for various PdCo/C catalysts.

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