



Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem
<http://www.journals.elsevier.com/journal-of-energy-chemistry/>

Active sites contribution from nanostructured interface of palladium and cerium oxide with enhanced catalytic performance for alcohols oxidation in alkaline solution

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ARTICLE INFO

Article history:

Received 27 November 2017

Revised 14 December 2017

Accepted 15 December 2017

Available online xxx

Keywords:

Alcohols oxidation

Fuel cells

Pd catalysts

Electrooxidation

CO stripping

ABSTRACT

Nanostructured interface is significant for the electrocatalysis process. Here we comparatively studied the electrooxidation of alcohols catalyzed by nanostructured palladium or palladium–cerium oxide. Two kinds of active sites were observed in palladium–cerium oxide system, attributing to the co-action of Pd–cerium oxide interface and Pd sites alone, by CO stripping technique, a structure-sensitive process generally employed to probe the active sites. Active sites resulting from the nanostructured interfacial contact of Pd and cerium oxide were confirmed by high resolution transmission electron microscopy and electrochemical CO stripping approaches. Electrochemical measurements of cyclic voltammetry and chronometry results demonstrated that Pd–cerium oxide catalysts exhibited much higher catalytic performances for alcohols oxidation than Pd alone in terms of activity, stability and anti-poisoning ability. The improved performance was probably attributed to the nanostructured active interface in which the catalytic ability from each component can be maximized through the synergistic action of bi-functional mechanism and electronic effect. The calculated catalytic efficiency of such active sites was many times higher than that of the Pd active sites alone. The present work showed the significance of valid nanostructured interface design and fabrication in the advanced catalysis system.

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1. Introduction

Nanostructured Pd-based catalysts are significant to the electrooxidation of alcohols, an important half reaction in direct alcohols fuel cells that are considered to satisfy the increasing demands of high power density at low cost for technological developments [1–6]. It has long been accepted that exploring highly efficient catalysts for alcohols oxidation is urgent for the current fuel cells technology development due to the usage of noble metals [7,8]. With this goal in mind, quite a lot of works have been done to reduce the noble metal loading and increase the activity and durability by exploring novel hybrid catalyst materials [9–13].

A bi-functional mechanism of alcohols electrooxidation based on a Pt–Ru material is well recognized, in which the Pt provides active sites for the adsorption and oxidation of alcohols molecular and the neighboring Ru offers the oxygen-containing species for the oxidation of intermediates produced during the alcohols oxidation [10,14,15]. The electronic effect in atomic scale from the

interaction of different components in the catalyst system is significant in understanding the performance improvements [16]. Deriving from the above mechanisms, noble metals like Pt and Pd in combination with the transition metal oxides were intensively developed and significant advances were made to push the development of fuel cells catalyst industries [17–20]. For example, platinum–nickel hydroxide was reported to have excellent catalysis activity and durability for methanol oxidation in alkaline solution, due to the combined contribution from each component and the electronic effect via interaction of individuals [21]; La₂O₃ can promote formic acid oxidation over Pd catalyst because of the improved electron transfer during electrochemical reaction [22]; other kind of metal oxides like Co₃O₄ [23], MnO₂ [24] and TiO₂ [25] have been demonstrated to exhibit improved catalytic activity and durability for alcohols oxidation.

It is happy to see many advanced catalyst materials proposed in recent years, however if we take a look at the work carefully, there are still some flaws or imperfection in understanding the origin of performance [26]. For the catalysts system proposed, the heterostructure of the active sites and neighboring promotion sites surely can guarantee the catalysis process of adsorption and charge transfer, and the promotion effect in all work was attributed to the

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40 synergistic effect of the catalyst components in the system. Unfor- 103
41 tunately, by surveying the literatures, we do not find directly 104
42 tance from the electrochemical measurements, though the connec- 105
43 tion interface was claimed visible in the microscopic images [27]. 106
44 Moreover, it is still not clear how the interface active sites con- 107
45 tributed to the improved activity. It is highly desirable that if we 108
46 could observe some clues from the electrochemical measurements 109
47 to confirm these active sites from the nano-interface contact and
48 analyze the contribution to the improved performance.

49 Pd-cerium oxide system was reported as a highly efficient 110
50 catalyst for alcohols oxidation according to the bi-functional 111
51 mechanism and electronic effect [28]. Because cerium oxide has 112
52 multi-valences that can provide enough oxygen-containing species 113
53 during the electrochemical oxidation process, it was thought as an 114
54 efficient assistant-catalyst in alcohols oxidation. Though the effect 115
55 of fabrication approaches was intensively studied and the promo- 116
56 tion effect of oxide was evident, probing the promotion effect in 117
57 depth is still going on due to the complicated effect in this catalyst 118
58 system that involves the metal oxide state, surface compositions, 119
59 electronic effect and so on [29,30]. Herein, back to our concerns, 120
60 there is no active sites evaluation in the catalyst characterization 121
61 or even no relevant reports to disclose the active sites contribution 122
62 to catalytic performance. In the current study, we re-scrutinized 123
63 the Pd-cerium oxide system for alcohols oxidation in the alka- 124
64 line solutions to probe the possible active sites contribution to 125
65 the catalytic performance improvement. In considering the multi- 126
66 ple valence states of cerium oxide, it was shortened as CeO_x in the
67 present work. A common approach for Pd based catalyst prepara-
68 tion was employed in which Pd nanoparticles were anchored on
69 the surface of hybrid support; with this method, different active
70 sites were anticipated to form by anchoring Pd particles on the car-
71 bon surface or CeO_x surface. The catalyst material was thoroughly
72 measured and characterized; as expected, we find the consistence
73 not only from the physical characterizations but also from the elec-
74 trochemical CO stripping measurements. We also for the first time
75 analyzed the activity contributions from the different active sites
76 presented in the system and found the active sites from nanostruc-
77 tured interface are more active and efficient in the electro-catalysis
78 process. The importance of forming nano-interface from multiple
79 components is emphasized for the highly active electrode materials
80 preparation. The results are significant in understanding the cataly-
81 sis mechanism and developing new hybrid nano-catalysts material.

82 2. Experimental

83 2.1. Preparation of Pd-CeO_x/C

84 The CeO_x/C support was prepared as follows: A given amount 128
85 of Ce₂O₃ was dissolved in 15 mL of concentrated HNO₃ and then 129
86 diluted in 100 mL mixed solution of ultrapure water and ethanol 130
87 (1:1 in volume ration). Then, a given amount of Vulcan XC-72 car- 131
88 bon was ultrasonically dispersed into the above solution, and the 132
89 solution was kept at room temperature (25 °C) under vigorous agi- 133
90 tation for 4 h. After stirring, 1 M NaOH and 0.5 M Na₂CO₃ solution 134
91 were added in turn into the mixture to form precipitates. Subse- 135
92 quently, the suspension was stirred overnight and finally filtered 136
93 and the solid was transferred to a tubular oven at 550 °C for 3 h 137
94 under the protection of N₂ to obtain a stable CeO_x/C support. 138

95 In the second step, the Pd-CeO_x/C catalyst was synthesized. 139
96 First, a given amount of CeO_x/C hybrid support and H₂PdCl₄ solu- 140
97 tion were ultrasonically dispersed in 50 mL of ethylene glycol. And 141
98 then the pH of the suspension was adjusted to about 11 by adding 142
99 1 M NaOH solution dropwise slowly under sonication. After that, 143
100 the suspension was kept at room condition for 1 h. The resulting 144
101 suspension was placed in the middle of a microwave oven operat-
102 ing at 700 W for 60 s on and 15 s off in turn for three times and

103 cooled to room temperature naturally. Finally, the suspension was 104
104 filtered, washed and dried overnight at 70 °C in a vacuum oven. 105
105 All solutions were prepared using Thermo Fisher Scientific (USA) 106
106 Co. Ltd. ultrapure water and analytical-grade reagents. For a valid 107
107 comparison, home-made Pd/C catalyst 20 wt% was also prepared 108
108 by the same approach. All of the materials were purchased and 109
109 used without further purification.

110 2.2. Physical characterizations

111 Transmission electron microscopy (TEM) and element mapping 112
112 analysis were conducted on a TECNAI G2 operating at 200 kV. Sam- 113
113 ples were sonicated and dispersed in ethanol and placed dropwise 114
114 onto a copper support grid for TEM observation.

115 Scanning electron microscopy (SEM) and energy dispersive X- 116
116 ray detector spectrum (EDS) measurements were performed with 117
117 an XL30 ESEM FEG field emission scanning electron microscope to 118
118 determine the morphology.

119 X-ray photoelectron spectroscopy (XPS) measurements were 120
120 carried out on an ESCALAB250Xi spectrometer with an Al K α ra- 121
121 diation source.

122 X-ray diffraction (XRD) measurements were performed with a 123
123 PW1700 diffractometer (Philips Co.) using a Cu K α ($\lambda = 1.5405 \text{ \AA}$) 124
124 radiation source operating at 40 kV and 40 mA. A fine powder sam- 125
125 ple was grinded, then put into the glass slide and pressed to make 126
126 a flat surface under the glass slide.

127 2.3. Electrochemical measurements

128 All the electrochemical measurements were carried out on an 129
129 INTERFACE 1000 potentiostat/galvanostat (GAMRY INSTRUMENTS 130
130 Co., USA) and a conventional three-electrode test cell was em- 131
131 ployed. The saturated calomel electrode (SCE, Hg Hg₂Cl₂) was used 132
132 as reference electrode. All of the potentials were relative to the SCE 133
133 electrode. A Pt plate with 10 cm² was used as a counter electrode. 134
134 A glassy carbon electrode coated by thin film catalyst (diameter 135
135 $d = 3 \text{ mm}$) was used as a working electrode.

136 Cyclic voltammetry measurements were carried out in 1 M 136
137 KOH electrolyte and purged with high-purity N₂ to remove 137
137 dissolved oxygen. Electrochemical experiments of methanol 138
138 oxidation were performed in 1 M KOH containing 1 M methanol 139
139 solution and ethanol oxidation was performed in 1 M KOH contain- 140
140 ing 1 M ethanol solution. All solution preparations were supplied 141
141 by ultrapure water. All glass electrodes were cleaned by polishing 142
142 with 0.05 μm alumina powder suspension (water) followed by 143
143 ultrasonic cleaning in deionized water before use. 144

145 2.4. Electrochemical pre-treatment

146 The catalyst ink was prepared by ultrasonically dispersing a 146
147 mixture containing 5 mg of catalyst, 950 μL of ethanol and 50 μL of 147
148 a 5 wt% Nafion solution. Next, 5 μL of the catalyst ink was pipetted 148
148 onto a pre-cleaned working electrode. 149

150 2.5. CO stripping

151 The adsorbed carbon monoxide (CO_{ad}) stripping voltammetry 151
152 was measured in a 1 M KOH solution. CO was purged into the KOH 152
153 solution for 15 min to allow the complete adsorption of CO onto 153
153 the catalyst when the working electrode was kept at -0.8 V (vs. 154
154 SCE), and excess CO in the electrolyte was purged out with N₂ for 155
155 15 min. The amount of CO_{ad} was evaluated by integration of the 156
156 CO_{ad} stripping peak, assuming 420 $\mu\text{C cm}^{-2}$ of coulombic charge 157
157 required for the oxidation of the CO monolayer. 158

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