Tailoring nanopores within nanoparticles of PtCo networks as catalysts for methanol oxidation reaction

Jieting Ding [a,d], Shan Ji [b*], Hui Wang [a], Bruno G. Pollet [c] and Rongfang Wang [a,d**]

[a] Institute of Chemical Engineering, Qingdao University of Science and Technology,

Qingdao, 266042, China

[b] College of Biological, Chemical Science and Chemical Engineering, Jiaxing

University, Jiaxing, 314001, China

[c] Centre for Renewable Energy, Department of Energy and Process Engineering,

Faculty of Engineering, Norwegian University of Science and Technology, NO-7491

Trondheim, Norway

[d] College of Chemistry and Chemical Engineering, Northwest Normal University,

Lanzhou 730070, China

Corresponding Authors:

Shan Ji (*): jissshan@126.com, Tel./fax: +86-572-82315109

Rongfang Wang (**): wrf38745779@126.com, Tel./fax: +86-931-7971533.

Abstract: It has been recently reported that engineering the pores within alloy nanoparticles leads to improvement in the electrochemical activity of nanoparticle catalysts due to the enhanced electrochemical active surface areas. However, to date, few works have reported the tailoring intraporosity within alloy nanoparticle networks. In this study, a different and innovative approach was adopted to yield a network-like PtCo catalyst composed of intraporous nanoparticles used a cotton-like PtCo

precursor material. It was found that the network-like structure and intrapores within the nanoparticles could co-evolve after careful controlled electrochemical dealloying, whereby Pt-rich surface was formed during the leaching out of Co in the first 13th potentiostatic cyclic voltammetry cycles from +0.056 to +1.256 V *vs.* RHE. Electrochemical data also showed that the mass and area activity of the obtained PtCo networks toward methanol oxidation reaction (MOR) was nearly 3.9, 2.0 and 2.1 times higher than that of commercial Pt/C, PtRu/C catalyst respectively, and much higher than that of Pt$_3$Co networks made of only solid nanoparticles. Moreover, it was observed that such networks exhibited high CO oxidation ability whilst maintaining high catalytic durability under an applied potential of +0.756 V *vs.* RHE. It was found that developing network-like catalysts composed of porous nanoparticles can be an efficient strategy to improve the catalytic activity and durability of fuel cell catalysts.

Keywords: PtCo alloy, dealloying, electrocatalyst, durability, methanol oxidation reaction.

1. Introduction

Platinum Group Metals (PGM)- and Pt-based nanomaterials are the most widely used anode and cathode electrocatalysts in low temperature fuel cells (e.g. PEMFC, DMFC etc), which are currently seen as promising energy storage devices to directly and efficiently convert the chemical energy to electrical energy. However, the prohibitive cost of platinum, accounting for over 55% of the total cost of low temperature fuel cell systems, the poor durability and the scarcity in supply largely hindered their large-scale practical applications and market deployment [1]. Therefore,

intense R&D efforts have been devoted to improve the inherent activity of Pt-based catalysts as well as reducing the Pt loading without compromising on the overall fuel cell performance [2]. Among these efforts, one efficient route is to create a porous structure of the electrocatalyst yielding large electrochemical surface area, high surface-to-volume ratio, and high gas permeability, in turns resulting in enhanced catalytic performance [3-6]. From the literature, it was found that network-like structures made of solid nanoparticles, such as PtNi, PtCo, PdP, have attracted great attention due to promising and enhanced catalytic performance [7-10]. Moreover, to further improve the catalytic performance, some successful strategies have been developed, for example, by adding non-metallic element such as P, tuning the atomic composition, and optimizing the particle size of the network-like catalysts [11-13].

Recently, nanoporosity in Pt-based alloy nanoparticles, formed via dealloying the alloy nanoparticle precursor, has often been reported and found to be an effective method to enhance the electrocatalytic activity [14-19]. This implies that the catalytic activity of the network-like electrocatalysts can be improved by forming porosity within the nanoparticles. On the other hand, porosity within nanoparticles does not evolve for all of PGM- and Pt-based nanoparticles because the initial content of the transition metals need to be high enough and the particle size of the Pt-based alloy nanoparticle precursor must be large enough for pore formation. For example, Snyder *et al.* and Oezaslan *et al.* reported that the particle size of $PtNi_3$ and $PtCo_3$ alloy nanoparticles had to reach a critical value of ca. 15 nm and ca. 30 nm respectively in order to yield full porosity within the nanoparticles [18, 20]. In the reported

network-like electrocatalysts made of alloy nanoparticles [8-11, 13, 21], particle diameters have been found to be below 10 nm, which are insufficient for forming stable porous structures. Therefore, to engineer porosity with the particles of the network structure at a nanoparticle scale, a suitable precursor must be carefully chosen.

In this study, we report a three-dimensional PtCo network-like structure assembled by the porous PtCo nanoparticles formed by electrochemical dealloying. Herein, the obtained PtCo nanoparticles is a porous network-like structure, which is different from the dense particles of the reported network-like structures [3-13]. In this work, the precursor PtCo particles is a cotton-like alloy, which is different from the dense solid alloy particles used in the previous reports [14-19]. Therefore, the restriction on the sizes of the alloy nanoparticle precursor is broken. This method could be extended to form other alloy with network-like structures assembled by porous nanoparticles. Methanol oxidation reaction (MOR) experiments were conducted on the as-prepared PtCo networks made of porous nanoparticles; it was found that the new material exhibited high catalytic activity than that of the commercial Pt/C, PtRu/C catalysts and the reference Pt_3Co networks composed of the solid nanoparticles.

2. Experimental

2.1 Synthesis

All reagents were of analytic grade, and ultrapure water was used throughout the experiments. Part one: To prepare the flocculent PtCo samples, a solution was prepared as follows: 4 mg $CoCl_2 \cdot 6H_2O$, 0.044 mL H_2PtCl_6 (20 mg mL^{-1}) were

dissolved in 60 mL water bubbled continuously with N_2. 10 mL 0.01 mol L^{-1} $NaBH_4$ solution in a constant funnel was added dropwise into the above solution under stirring and N_2 bubbling conditions. Nitrogen acts as a protective gas throughout the reaction, reducing the formation of cobalt oxides. After chemical reaction for 20 min, the resultant precipitate was collected by filtration, then washed with deionized water several times and kept in an ethanol solution. Part two: the electrochemical etching method was used to prepare the network structured PtCo alloy. The electrode loaded precursor was dealloyed via cyclic voltammetry, which was carried out in N_2-saturated 0.1 mol L^{-1} $HClO_4$ electrolyte with a scan rate of 0.05 V s^{-1} in the potential range from 0.056 to 1.256 V vs. RHE. With the increase of the number of cycles, the surface of catalyst went through three stages: initially dissolution of Co occurs, followed by the gradual exposure of Pt atoms, and finally Pt atoms accumulated on the surface.

2.2 Physical and Electrochemical Characterizations

The catalysts were characterized by recording their XRD patterns on a Shimadzu XD–3A (Japan), using filtered Cu-Kα radiation (λ = 0.15418 nm), generated at 40 kV and 30 mA. Scans for 2θ values were recorded at 4° min^{-1} between 25° and 90°. Transmission electron micrographs (TEM), high angle annular dark field scanning transmission electron microscopy (STEM) images of the catalysts were taken on a JEOL (JEM-2000 FX) microscope operating at 200 kV. Energy dispersive spectroscopy in the STEM mode was employed for determining elemental composition of either individual nanoparticle or several nanoparticles. X-ray

5

photoelectron spectroscopy (XPS) (Thi-5702 America) with a monochromatic Al Kα X-ray source (hm = 29.35 eV). The bulk composition of the samples was determined by a Varian 720 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). The BJH method was used for analyzing the full range of pore size distribution based on the desorption isotherms obtained on a Quantachrome Autosorb-1 volumetric analyzer.

Electrochemical experiments on the catalysts were performed using the electrochemical work station potentiostat/galvanostat CHI 650D. A typical three-electrode electrochemical cell was used to determine important electrochemical parameters. The counter (CE) and reference (RE) electrodes were a platinum wire and a Ag/AgCl (saturated KCl) electrode, respectively. The working electrode (WE) was a glassy carbon disc ($\varnothing$ = 5 mm). The thin-film electrode method was used and electrodes were prepared as follows: 2 mg of catalyst was dispersed ultrasonically in 0.4 mL Nafion®/ethanol (0.25% Nafion®) solution for 15 min. 8 µL of the dispersion was transferred onto the glassy carbon disc using a pipette, and then dried in air. For CO stripping experiments, CO was adsorbed on the working electrode by bubbling it through the electrochemical cell for 5 min, and then the working electrode was inserted into another electrochemical cell containing a nitrogen-purged 0.1 mol L^{-1} HClO$_4$ solution.

3. Results and Discussion

The cotton-like PtCo precursors were synthesized by the co-reduction of H$_2$PtCl$_6$ and CoCl$_2$ with NaBH$_4$ in a solution bubbled with N$_2$ at ambient temperature. The

physical characterization of the as-prepared PtCo precursor was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In the XRD curve for the PtCo precursor (Fig. 1), a broad peak is observed at $2\theta \approx 45°$, indicating the presence of an amorphous structure of the PtCo precursor [22].

The SEM image of the PtCo precursor shown in Fig. 2a displays a cotton-like morphology on a large scale. Fig. 2b highlights further details of the coexistence of cotton-like feature and particle-like shape, whereby the particles are covered by cotton-like layers, as evidenced in the TEM image (Fig. 2c). Elemental distribution was analyzed by electron energy loss spectroscopy (EELS) (area displayed in the SETM image in Fig. 2e). The EELS element maps of Co (Fig. 2e) and Pt (Fig. 2f), and their overlapped map (Fig. 2g) indicate that Pt is grouped in the particle area, and Co is distributed throughout all other regions. This observation also indicates that the PtCo precursor is composed of the alloy structure with a Co-rich surface.

The synthesis process of the PtCo networks was performed via the electrochemical cycling voltammetric dealloying in the potential range of +0.056 - +1.256 V *vs.* RHE at a scan rate of 0.05 V s^{-1} applied to an immobilized cotton-like PtCo precursor electrode. Fig. 3 shows the evolution of the CV change at various cycling voltammetric cycles. Fig. 3a shows a distinct oxidation peak at the first (1st) CV scan representing the dissolution of surface Co from the precursor surfaces. The first CV scan also indicates a Co-rich surface in the precursor, which is in good agreement with our findings based on the EELS element maps. As potential cycling continues, it

can be observed that the Co oxidation peak decreases indicating a gradual removal of Co atoms from the precursor, whilst the hydrogen desorption/absorption peaks can be clearly observed at the fourth (4th) cycle, implying that the Pt atoms are exposed on the surface. From the 4th to the 13th cycle (Fig. 3b), the hydrogen desorption/absorption peak heights increase, indicating an enrichment process of the Pt atoms onto the surface accompanied with the continuous dissolution of Co atoms. The almost constant height of the hydrogen desorption/absorption peaks after the 13th cycle (Fig. 3c) suggests the formation of a complete Pt shell. From the CV experiments, it can be suggested that a three-step process exists for the formation of PtCo networks from the cotton-like PtCo precursor based on the surface composition, as illustrated in the schematic in Fig. 4, containing (i) a Co-rich surface, (ii) a PtCo-alloyed surface, and (iii) a Pt-rich surface. To further elucidate the electrochemical activity of the newly as-prepared electrocatalyst material, two samples were collected after the 4th, 13th CV cycle for further study.

PtCo samples (after 4th cycle and 13th cycle) were characterized by SEM and TEM. As presented in Fig. 5a, the cotton-like Co on the surface of the sample has been etched. In Fig. 5b, the network-like morphology in the PtCo sample was completely formed. The high-magnification SEM image (Fig. 5b') indicates that the networks are composed of ca. 25 nm aligned nanoparticles. The TEM image in Fig. 5c again confirms the presence of a network-like structure on a large scale. The enlarged TEM image in Fig. 5d shows the presence of (i) ellipse-like shape nanoparticles with diameters of ca. 20~30 nm, and (ii) white bright areas within the nanoparticles. The

high resolution TEM image in Fig. 5e indicates that these white bright zones (marked by the red arrows) are irregular pores, confirming that the PtCo nanoparticles are porous structures, (also observed from the STEM image in Fig. 5f). This finding indicates that the PtCo networks made of porous nanoparticles can be formed using the cotton-like PtCo precursor by the electrochemical dealloying. Fig. 5g shows the distribution profiles of Pt and Co elements in a typical regional (the red line in the STEM image in Fig. 5f) exhibiting porous nanoparticles. It can be observed that the width of the peaks of Pt extend to that of Co, indicating that the Pt layers with a thickness of ca. 0.8 nm was formed on the outer surface of the nanoparticles, which is in very good agreement with the CV features. The Pt-rich surface is also evidenced by X-ray photoelectron spectroscopy (XPS) analysis. As shown in Fig. 6, the weak Co signal compared to that of Pt suggests the enrichment of Pt on the surface. The bulk composition of the obtained PtCo networks analyzed by ICP-OES was found to be 5.2:2.1.

The crystal structure of PtCo (4th cycle) and PtCo networks were characterized by XRD, which is presented in Fig. 1. In the two curves, four distinct diffraction peaks at ca. 40.4 ^{o}, 45.9 ^{o}, 68.1 ^{o}, and 81.8^o can be observed, corresponding to (111), (200), (220), and (311) diffractions respectively. It was found that the character of a polycrystalline Pt had a face-centered cubic (fcc) phase [23]. It can also be seen that the diffraction peaks of the as-prepared PtCo networks shift to the higher 2θ degree compared to pure Pt, suggesting that some Pt atoms were displaced by the smaller Co atoms, leading to the small lattice parameter of PtCo networks.

In order to further prove that porous structure could be formed by electrochemical etching, cotton-like precursor was directly immersed in 0.1 M HClO$_4$ for several hours. As shown in Fig. 7a and Fig. 7b, no porous structure was found and the network structure was also collapsed. Therefore, electrochemical etching is the key to form the porous structure. The information of pores was further characterized by N$_2$ isotherm analysis. The appearance of hysteresis loop in Fig. 7c indicates the existence of mesopores in PtCo networks. The pore size distribution (Fig.7c) shows that the pores in PtCo networks include micropores and mesopores, which is consistent with the TEM result.

The electrochemical properties of the as-prepared PtCo networks were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) experiments. For comparison purposes, the commercial Pt/C，PtRu/C (20 wt% Johnson Matthey) catalyst and the network-like Pt$_3$Co catalyst composed of solid nanoparticles and synthesized according to the method in Reference [8], were used as reference materials. Fig. 8a shows the CVs obtained in 0.1 mol L^{-1} HClO$_4$ on the as-prepared PtCo, Pt$_3$Co, Pt/C and PtRu/C electrodes. For the four samples, typical CV features of Pt surface are observed, i.e. hydrogen desorption/adsorption peaks in the low potential range, metal oxidation/oxide reduction wave/peak in the high potential range, and a flat double layer in between [24]. To estimate the active sites on the catalyst surface, the electrochemical active surface area (*ECSA*) of the catalyst was calculated according to equation 1 [25]:

$$ECSA \, (\mathrm{m^2 g^{-1}_{Pt}}) = Q_H/(2.1 \times m_{Pt}) \qquad (1)$$

where Q_H (C) represents the average charge of the hydrogen adsorption/desorption area, m_{Pt} (g) is the Pt loading on the electrode, and 2.1 is the charge (C m^{-2}) required to oxidize a monolayer of hydrogen on the Pt surface. The calculated *ECSA*s of the as-prepared PtCo, Pt$_3$Co, Pt/C and PtRu/C samples are 54.4, 53.1, 52.0 and 53.6 m^{2}g^{-1}$_{Pt}$ respectively. Compared to the Pt$_3$Co, Pt/C and PtRu/C samples, the as-prepared PtCo sample exhibited a slight enhanced *ECSA*.

Fig. 8b,c show the CVs of the four catalysts in 0.5 mol L^{-1} N$_2$-saturated 0.5 mol L^{-1} CH$_3$OH + 0.1 mol L^{-1} HClO$_4$ solution. The current density was normalized by the Pt mass (Fig. 8b) and the *ECSA* (Fig. 8c) on the electrodes respectively. It can be seen from the two figures that the current density in the overall potential range on the PtCo electrode is higher than those on the Pt$_3$Co, Pt/C and PtRu/C electrodes. The forward oxidation peak current on the PtCo catalyst in Fig. 7b was found to be 0.960 A mg^{-1}$_{Pt}$ at ca. +0.916V *vs.* RHE, i.e. 2.1, 3.9 and 2.0-fold higher than those found for Pt$_3$Co (0.466 A mg^{-1}$_{Pt}$ at 0.966 V *vs.* RHE), Pt/C (0.247 A mg^{-1}$_{Pt}$ at +0.996 V *vs.* RHE) and PtRu/C (0.491 A mg^{-1}$_{Pt}$ at +0.965 V *vs.* RHE) respectively. When the current was scaled by the *ECSA*, the forward oxidation peak on the PtCo catalyst in Fig. 8c reached 1.76 mA cm^{-2}$_{Pt}$, 2.0, 3.7 and 1.9-fold higher than those obtained for Pt$_3$Co (0.88 mA cm^{-2}$_{Pt}$), Pt/C (0.47 mA cm^{-2}$_{Pt}$) and PtRu/C (0.91 mA cm^{-2}$_{Pt}$) respectively. This finding indicates a better catalytic activity of the as-prepared PtCo catalyst toward the MOR. To further demonstrate the catalytic superiority of the as-prepared electrocatalysts, methanol oxidation activity of the catalysts was studied by determining the onset potential of the MOR through conventional linear sweep

voltammogram (LSV). As shown in Fig. 8d, the lowest MOR onset potential of +0.506 V *vs.* RHE was found on the as-prepared PtCo catalyst, which is +50 , +100 and +40 mV more negative than that of the Pt_3Co (+0.556 V *vs.* RHE) , Pt/C (+0.606 V *vs.* RHE) and PtRu/C (+0.545 V *vs.* RHE) electrodes respectively. In terms of both the oxidation peak current and the onset potential for MOR, the as-prepared PtCo catalyst exhibited better catalytic activity compared to the Pt_3Co, Pt/C and PtRu/C catalysts owing to the advantage of intraporous structure within the nanoparticles and the Pt-rich surface.

The catalytic durability for MOR on the as-prepared PtCo, Pt_3Co, Pt/C and PtRu/C catalysts was investigated by chronoamperometry (CA) in a 0.1 mol L^{-1} $HClO_4$ + 0.5 mol L^{-1} CH_3OH solution at an applied potential of +0.756 V *vs.* RHE. As shown in Fig. 8e, for the four plots, the current densities decrease with time, resulting from the inactivation of the 'poisoned' surface active sites by the accumulative toxic intermediates. The current densities at the end of 1,000 s in Fig. 8f were determined to be 1.15 mA cm^{-2}_{geo} for the as-prepared PtCo, 0.75 mA cm^{-2}_{geo} for the Pt_3Co, 0.66 mA cm^{-2}_{geo} for the Pt/C, and 0.87 mA cm^{-2}_{geo} for the PtRu/C. The oxidation current density on the as-prepared PtCo catalyst electrode at 1,000 s was found to be 1.53, 1.74 and 1.32 times higher than those determined on Pt_3Co, Pt/C and PtRu/C respectively.

In CO-stripping experiments, as shown in Fig.9, an oxidation peak appears between +0.696~+1.196 V *vs.* RHE during the first scan, corresponding to CO oxidation. In the subsequent scan, CO oxidation peak disappeared, indicating that the adsorbed CO

12

was completely removed by the oxidation reaction. It can also be observed that the CO peak on the PtCo electrode located at +0.726 V *vs.* RHE is more negative than that of the Pt$_3$Co (+0.746 V *vs.* RHE), Pt/C (+0.826 V *vs.* RHE) and PtRu/C (+0.744 V *vs.* RHE) indicating a more facile CO removal on the PtCo catalyst, and hence, an improved oxidation capacity for CO in practice. These results imply that the as-prepared PtCo catalyst materials have a strong oxidation capacity for the poisonous intermediates produced during the methanol oxidation process. This finding is in excellent agreement with that obtained from CA experiments.

4. Conclusions

Network-like PtCo made of porous nanoparticles were fabricated using the cotton-like PtCo precursor via the electrochemical dealloying method. During dealloying, Co dissolution triggered the formation of the intrapores within the nanoparticles coupled with the formation of the network-like structure. Moreover, it was found that areas of Pt atoms rich on the surface of the porous PtCo nanoparticles were formed. The as-prepared PtCo catalyst displayed markedly improved activity for MOR (mass- and area- activity, low onset potential) and durability compared to the Pt$_3$Co networks made of solid nanoparticles, Pt/C and PtRu/C catalysts. It is reasonable to state that the obtained PtCo networks could be a potential candidate for MOR catalyst in direct methanol fuel cells. Furthermore, our proposed synthesis strategy could be extended to explore other alloy networks made of porous nanoparticles, which could lead to promising candidates for highly active catalysts for other electrochemical reactions.

Acknowledgment

References

[1] H. Zhang, M. Jin, Y. Xia, Enhancing the catalytic and electrocatalytic properties of Pt-based catalysts by forming bimetallic nanocrystals with Pd, Chemical Society Reviews, 41 (2012) 8035-8049.

[2] H.-l. Liu, F. Nosheen, X. Wang, Noble metal alloy complex nanostructures: controllable synthesis and their electrochemical property, Chemical Society Reviews, 44 (2015) 3056-3078.

[3] C. Zhu, S. Guo, S. Dong, Rapid, general synthesis of PdPt bimetallic alloy nanosponges and their enhanced catalytic performance for ethanol/methanol electrooxidation in an alkaline medium, Chemistry- A European Journal, 19 (2013) 1104-1111.

[4] X.-Y. Liu, Y. Zhang, M.-X. Gong, Y.-W. Tang, T.-H. Lu, Chenab，Yu, L. Jong-Min, Facile synthesis of corallite-like Pt–Pd alloy nanostructures and their enhanced catalytic activity and stability for ethanol oxidation, Journal of Materials Chemistry A, 2 (2014) 13840-13844.

[5] Y. Xu, B. Zhang, Recent advances in porous Pt-based nanostructures: synthesis and electrochemical applications, Chemical Society Reviews, 43 (2014) 2439-2450.

[6] M. Wang, X. Song, Q. Yang, H. Hua, S. Dai, C. Hu, D. Wei, Pt nanoparticles supported on graphene three-dimensional network structure for effective methanol and ethanol oxidation, Journal of Power Sources, 273 (2015) 624-630.

[7] J. Zhang, Y. Xu, B. Zhang, Facile synthesis of 3D Pd-P nanoparticle networks with enhanced electrocatalytic performance towards formic acid electrooxidation, Chemical Communications, 50 (2014) 13451-13453.

[8] Y. Xu, Y. Yuan, A. Ma, X. Wu, Y. Liu, B. Zhang, Composition-Tunable Pt-Co Alloy Nanoparticle Networks: Facile Room-Temperature Synthesis and Supportless Electrocatalytic Applications, ChemPhysChem, 13 (2012) 2601-2609.

[9] Y. Xu, S. Hou, Y. Liu, Y. Zhang, H. Wang, B. Zhang, Facile one-step room-temperature synthesis of Pt3Ni nanoparticle networks with improved electro-catalytic properties, Chemical Communications, 48 (2012) 2665-2667.

[10] L. Zhang, D. Lu, Y. Chen, Y. Tang, T. Lu, Facile synthesis of Pd–Co–P ternary alloy network nanostructures and their enhanced electrocatalytic activity towards hydrazine oxidation, Journal of Materials Chemistry A, 2 (2014) 1252-1256.

[11] Y. Ma, H. Wang, W. Lv, S. Ji, B.G. Pollet, S. Li, R. Wang, Amorphous PtNiP particle networks of different particle sizes for the electro-oxidation of hydrazine, RSC Advances, 5 (2015) 68655-68661.

[12] Y. Ma, R. Wang, H. Wang, J. Key, S. Ji, Room-temperature synthesis with inert bubble templates to produce "clean" PdCoP alloy nanoparticle networks for enhanced hydrazine electro-oxidation, RSC Advances, 5 (2015) 9837-9842.

[13] R. Wang, Y. Ma, H. Wang, K. Julian, S. Ji, Gas-liquid interface-mediated room-temperature synthesis of "clean" PdNiP alloy nanoparticle networks with high catalytic activity for ethanol oxidation, Chemical Communications, 50 (2014) 12877-12879.

[14] D. Wang, Y. Yu, H.L. Xin, R. Hovden, P. Ercius, J.A. Mundy, H. Chen, J.H. Richard, D.A. Muller, F.J. DiSalvo, Tuning oxygen reduction reaction activity via controllable dealloying: a model study of ordered Cu_3Pt/C intermetallic nanocatalysts, Nano Letters, 12 (2012) 5230-5238.

[15] L. Gan, M. Heggen, S. Rudi, P. Strasser, Core-shell compositional fine structures of dealloyed Pt_xNi_{1-x} nanoparticles and their impact on oxygen reduction catalysis, Nano Letters, 12 (2012) 5423-5430.

[16] C. Du, M. Chen, W. Wang, G. Yin, Nanoporous PdNi Alloy Nanowires As Highly Active Catalysts for the Electro-Oxidation of Formic Acid, ACS Applied Materials & Interfaces, 3 (2010) 105-109.

[17] L. Chen, H. Guo, T. Fujita, A. Hirata, W. Zhang, A. Inoue, M. Chen, Nanoporous PdNi Bimetallic Catalyst with Enhanced Electrocatalytic Performances for Electro-oxidation and Oxygen Reduction Reactions, Advanced Functional Materials, 21 (2011) 4364-4370.

[18] M. Oezaslan, M. Heggen, P. Strasser, Size-Dependent Morphology of Dealloyed Bimetallic Catalysts: Linking the Nano to the Macro Scale, Journal of the American Chemical Society, 134 (2011) 514-524.

[19] C. Poochai, W. Veerasai, E. Somsook, S. Dangtip, The influence of copper in dealloyed binary platinum–copper electrocatalysts on methanol electroxidation catalytic activities, Materials Chemistry and Physics, 163 (2015) 317-330.

[20] J. Snyder, I. McCue, K. Livi, J. Erlebacher, Structure/processing/properties relationships in nanoporous nanoparticles as applied to catalysis of the cathodic oxygen reduction reaction, Journal of the American Chemical Society, 134 (2012) 8633-8645.

[21] H. Li, Y.-J. Li, L.-L. Sun, X.-L. Zhao, One-step, template-free electrochemical preparation of three-dimensional porous Au nanowire network and its enhanced activity toward methanol electrooxidation, Electrochimica Acta, 108 (2013) 74-78.

[22] Y. Ma, R. Wang, H. Wang, V. Linkov, S. Ji, Evolution of nanoscale amorphous, crystalline and phase-segregated PtNiP nanoparticles and their electrocatalytic effect on methanol oxidation reaction, Physical Chemistry Chemical Physics, 16 (2014) 3593-3602.

[23] R. Wang, J. Jia, H. Wang, Q. Wang, S. Ji, Z. Tian, CNx-modified Fe_3O_4 as Pt nanoparticle support for the oxygen reduction reaction, J Solid State Electrochem, 17 (2013) 1021-1028.

[24] R. Wang, K. Wang, H. Wang, Q. Wang, J. Key, V. Linkov, S. Ji, Nitrogen-doped carbon coated ZrO2 as a support for Pt nanoparticles in the oxygen reduction reaction, International Journal of Hydrogen Energy, 38 (2013) 5783-5788.

[25] X.T. Zhang, H. Wang, J.L. Key, V. Linkov, S. Ji, X.L. Wang, Z.Q. Lei, R.F. Wang, Strain Effect of Core-Shell Co@Pt/C Nanoparticle Catalyst with Enhanced Electrocatalytic Activity for Methanol Oxidation, Journal of the Electrochemical Society, 159 (2012) B270-B276.