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Electrodeposited Pd-Co catalyst for direct methanol fuel cell electrodes: Preparation and characterization

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Abstract

Pd-Co alloy has been recently proposed as a catalyst for the cathode of direct methanol fuel cells with both excellent oxygen reduction activity and methanol tolerance, hence electrodeposition of this alloy is an attractive approach for synthesizing porous metal electrodes with high methanol tolerance in direct methanol fuel cells. In this study, we electrodeposited two types of Pd-Co films onto Au substrates by applying different current density (-10 or -200 mA cm⁻²); and then characterized them in terms of morphology, composition, crystal structure, and catalytic activity. Pd-Co deposited at -10 mA cm^{-2} was smooth and possessed smaller particles (ca. 10 nm), while that at -200 mA cm^{-2} was dendritic (or rough) and possessed larger particles (ca. 50 nm). Both the Pd-Co alloys were found to be almost the same structure, i.e. a solid solution of ca. Pd₇Co₃ with Pd-skin, and also confirmed to possess comparable activity in oxygen reduction to Pt (potential difference at 1.0 µA cm⁻² was 0.05 V). As for methanol tolerance, cell-voltage was not influenced by addition of 1 mol dm⁻³ methanol to the oxidant solution. Our approach provides fundamental technique for synthesizing Pd-Co porous metal electrodes by electrodeposition.

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Keywords: Pd-Co alloy; Electrodeposition; Oxygen reduction catalyst; Direct methanol fuel cells; Methanol tolerance

1. Introduction

In polymer electrolyte fuel cells, more effective catalysts are strongly required for commercialization, hence the materials and also their preparation methods have been studied extensively. Metal alloys [1–3], metal porphyrins [4,5], and other metal compounds [6,7] as well as their preparation methods based on thermal, chemical, and/or electrochemical treatment have been developed. Those materials are generally synthesized as nanoparticles for obtaining higher specific surface area, hence metal-alloy nanoparticles have been regarded as the most active catalyst so far [1-3].

Those nanoparticles are required to be formed into porous electrodes for effectively promoting reactions of fuel cells [8]. Conventionally, the porous structures have been prepared by

simply casting a mixture of catalyst particles and binder onto current collectors [8]. Recently, some sophisticatedly structured current-collectors, e.g. metal-mesh electrodes [9] and microelectrodes [10–13], have been studied for achieving better fuel-cell performance. They require catalysts to be synthesized directly and selectively onto the current collectors, thus, electrodeposition has been applied for preparing electrodes. Electrodeposition is also appropriate to synthesizing ordered porous materials with templates, e.g. mesoporous metals [14-16] and macroporous metals [15]. Therefore, electrodeposition is an attractive method for preparing electrodes for fuel cells.

Recently, Pd-based alloys have been reported to be oxygen reduction reaction (ORR) catalysts with excellent methanol tolerance [3,17–26]. The tolerance is important to DMFCs, because methanol permeating through the electrolyte membrane from anode is oxidized on ORR catalysts at cathode, and thus voltage as well as fuel-efficiency is degraded [27,28]. So far, the Pd-based ORR catalysts have been synthesized as nanoparticles or smooth films, not as porous metal catalysts to the best of our knowledge [3,17–26].

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Among the alloys, we focused on Pd-Co alloy, because they are possibly synthesized by electrodeposition as reported in the field of magnetic materials [29,30] or thin-coating materials [31]. Nonetheless, as oxygen reduction catalysts, only a preliminary evaluation on ORR activity was reported on electrodeposited Pd-Co alloy [21].

In this study, we electrodeposited and characterized Pd-Co alloys. Two different current densities were applied to obtain different surface morphology: rough and smooth; rough surface is directly applicable as porous electrode; smooth surface is suitable for template method. Compositions in the deposits should be less-dependent on current densities for obtaining highly active composition (i.e. Pd_7Co_3 [3,17–26]) easily; hence we applied an electrodeposition bath where the deposition potentials of Pd and Co are almost the same according to a literature [31]. Our approach is expected to extend application of Pd-Co catalyst to porous metal electrodes.

2. Experimental

Two types of Pd-Co films were electrodeposited onto Au substrates by applying different current densities, and then, characterized with respect to morphology, composition, crystal structure, and catalytic activity. In addition, performance of the Pd-Co during fuel cell operation was also evaluated.

2.1. Electrodeposition of the catalysts

The bath composition for electrodepositing Pd-Co and detail conditions are tabulated in Table 1. Electrodeposition was carried out on a flat Au electrode (deposited on a silicon substrate, 0.13 cm^2) by applying constant current for control-ling deposition rate to produce different films: low current density, -10 mA cm^{-2} , for smooth film; high current density, -200 mA cm^{-2} , for rough film. The former and the latter are named Pd-Co-10 and Pd-Co-200, respectively. Potentials shown in this paper are referred to a Ag/AgCl (KCl saturated).

For comparison, pure Pd and pure Pt were also electrodeposited. The Pd was electrodeposited at -1 mA cm^{-2} (600 s) in a bath containing only the palladium salt and the NH₄Cl shown in Table 1. The Pt was electrodeposited at -1 mA cm^{-2} (600 s) in a bath containing H₂PtCl₆ (0.02 mol dm⁻³).

 Table 1

 Bath composition and conditions for electrodepositing Pd-Co alloy

Reagent	Concentration (mol dm^{-3})
[Pd(NH ₃) ₄]Cl ₂	0.076
CoCl ₂ ·6H ₂ O	0.034
NH ₄ Cl	0.078
Malonic acid	0.120
pH	9.1 (adjusted by NH ₄ OH)
Temperature	Room temperature
Current density	$-10 \text{ or } -200 \text{ mA cm}^{-2}$
Deposition time	60 s

2.2. Characterization of the Pd-Co films

The Pd-Co films (as-deposited) were characterized in terms of morphology, composition, and crystal structure. Morphology was observed with a field emission-scanning electron microscope (FE-SEM, S-5500, Hitachi) at 5.0 kV. Bulk composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, IRIS-AP, Thermo Fisher Scientific) after dissolving the samples in aqua regia. Surface was investigated by X-ray photoelectron spectroscopy (XPS, JPS-9010TR, JEOL) applying MgK radiation (10 kV, 10 mA). Elemental depth profile was evaluated by glow discharge-optical emission spectrometry (GD-OES, GDA750, Rigaku). Crystal structures were analyzed by means of X-ray diffractmetry (XRD, inplane, RINT-TTRIII, Rigaku) applying Cu K α radiation (50 kV, 300 mA).

2.3. Electrochemical properties of the Pd-Co films

Electrochemical properties of the deposits were evaluated with respect to oxygen reduction activity, methanol tolerance, and response in acid media. Oxygen reduction activity was evaluated by linear sweep voltammetry (LSV) from the open circuit potential to 0.2 V vs. Ag/AgCl at 1 mV s⁻¹ in an oxygen-saturated sulfuric acid (0.5 mol dm⁻³). Methanol tolerance was evaluated by LSV in the same conditions as oxygen reduction activity measurements except for addition of methanol (1 mol dm⁻³) to the solution. Electrochemical responses were evaluated by cyclic voltammetry (CV, -0.2 to 1.0 V, 50 mV s⁻¹) in a nitrogen-saturated sulfuric acid (0.5 mol dm⁻³). All the properties were evaluated in a conventional three-electrode cell (the reference electrode: Ag/AgCl, the counter electrode: a Au wire) using a computer-controlled potentiostat (PARSTAT 2273, Princeton Applied Research) at 30 °C.

2.4. Activity of the Pd-Co during fuel cell operation

Using our µ-DMFC [10-12] as an example device, we investigate activity of the Pd-Co during fuel cell operation [32]. The μ -DMFC was fabricated on a silicon substrate with micro electromechanical systems (MEMS) technology, following our previous reports [10–12]. The μ -DMFC consists of two parallel microchannels with Au current collectors and thus catalysts should be selectively deposited onto the Au electrode (0.0091 cm²) in micrometer size. Onto the cathode current collector Pd-Co or Pt was electrodeposited, and onto the anode current collector Pt-Ru was electrodeposited. Pd-Co was deposited by applying constant current (-200 mA cm^{-2} , 5 s). The time, 5 s, was the loading amount optimized in terms of mass flow in the microchannel. Pt or Pt-Ru was deposited by applying pulse current (on: -50 mA cm^{-2} , 0.1 s; off: 0.5 s; 2 C cm $^{-2}$) for uniform deposition onto the microchannel in bathes reported previously [12]. For Pt-Ru preparation, 1 C cm^{-2} of Pt-Ru was deposited onto $1 \,\mathrm{C}\,\mathrm{cm}^{-2}$ of Pt because this process possibly reproduces an active Pt-Ru catalyst for the microchannel.

The cell performance was evaluated after the microchannels were covered up with a Nafion 112 (DuPont) membrane for

enabling ion transport between the electrodes. Current–voltage curves were recorded on a computer-controlled galvanostat with supplying a methanol solution $(1 \text{ mol } \text{dm}^{-3})$ containing sulfuric acid $(0.5 \text{ mol } \text{dm}^{-3})$ to the anode channel and an oxygen saturated sulfuric acid solution $(0.5 \text{ mol } \text{dm}^{-3})$ to the cathode channel using syringe pumps. To evaluate methanol tolerance of the Pd-Co catalyst during cell operation, current–voltage curves with adding 1 mol dm⁻³ methanol to the cathode solution was also evaluated.

3. Results and discussion

3.1. Electrodeposition of Pd-Co

We successfully obtained a shiny silver-colored film (Pd-Co-10) and a matt black film (Pd-Co-200) on the Au substrates. As preliminary test, we checked the color of deposits changed around -23 mA cm^{-2} . To obtain sufficiently rough surface, we applied excessively high current density, -200 mA cm^{-2} .

Current efficiency in the depositions of Pd-Co-10 and Pd-Co-200 are respectively calculated at 87% and 74% by means of ICP-AES. The decreases of the efficiency are probably attributed to hydride generation, hydrogen evolution, and/or oxygen reduction according to a literature on the Pd electrodeposition [33]. Potentials during deposition (shown in Fig. 1) of Pd-Co-10 (ca. -0.75 V) and Pd-Co-200 (ca. -2.0 V, fluctuated) were lower than the Nernst potential of hydrogen evolution (-0.74 V) of the bath (pH 9.1). These results suggest the relatively low efficiency of Pd-Co-200 is attributed to hydrogen evolution, indeed, we observed bubbles during Pd-Co-200 deposition.

3.2. Characterization

3.2.1. Compositions

Bulk compositions of Pd-Co-10 and Pd-Co-200 were determined by ICP-AES as $Pd_{66}Co_{34}$ and $Pd_{75}Co_{25}$, respectively. Thus, we successfully obtained the highly active composition (Pd_7Co_3) in oxygen reduction [3,17-26].



Fig. 1. Deposition potentials of Pd-Co-10 (at 10 mA cm^{-2}) and Pd-Co-200 (at 200 mA cm^{-2}).



Fig. 2. GD-OES of Pd-Co-10: Pd (black line), Co (grey line), and Au (dotted line). The inset shows depth profiles of molar fraction on Pd and Co.

GD-OES for Pd-Co-10 are shown in Fig. 2. The spectra indicate that Pd and Co were deposited in a constant ratio except for the Co-rich region near the Au electrode (the prepeaks within 0.2 s is attributed to the system of GD-OES [34]). Elemental depth profile (inset) was calculated using the thickness of 190 nm (FE-SEM) and the bulk composition,



Fig. 3. XPS of Pd-Co-10: Pd-3d (a) and Co-2p (b). The vertical dotted lines refer to Pd- $3d_{5/2}$ of pure Pd and Co- $2p_{3/2}$ of pure Co [40].

assuming that the etching rate was constant, and also that the interaction among elements was negligible [35]. Compositions are roughly estimated as about Pd_7Co_3 for the depth from 10 to 100 nm. Pd composition within 10 nm increases to the surface, hence we investigate the surface composition by XPS.

XPS of Pd-Co-10 are shown in Fig. 3 (XPS of Pd-Co-200 were almost the same). The peak area of Pd is clearly larger than that of Co, that is, the surface is considered to be Pd rich even taking sensitivity factors into consideration (the sensitivity factor of Pd-3d is 2–3 times higher than that of Co-2p [36]). This result probably indicates the formation of Pd-skin reported in the case of Pt alloys [37,38]. The Pd skin is probably rationalized in terms of thermodynamics with the alloy segregation theory [39] or replacement of surface Co by Pd in the bath after electrodeposition.

The surface Pd and Co are found to be metallic, not oxide, by comparing experimental binding energies (Pd- $3d_{5/2}$: 334.7 eV, Co- $2p_{3/2}$: 777.4 eV) to those of a literature (Pd- $3d_{5/2}$: 334.4 eV, Co- $2p_{3/2}$: 781.5 eV) [40]. As for the binding energy of Co, the shift of $2p_{3/2}$ peak to lower energy suggests alloying of Co with Pd [40].



Fig. 4. XRD patterns of PdCo-10 and Pd-Co-200. The vertical dotted lines refer to the diffraction angles of pure Pd. The weak diffraction peak marked with * in Pd-Co-200 is attributed to the Au substrate.

3.2.2. Crystal structure

XRD patterns of Pd-Co-10 and Pd-Co-200 are shown in Fig. 4. The vertical dotted lines show the diffraction angles of the fcc Pd lattice referred to JCPDS-ICDD: 40.2° for (1 1 1), 46.7° for (2 0 0), and 68.1° for (2 2 0). Peaks of Pd-Co-10 (40.6° , 47.1° , and 69.0°) and Pd-Co-200 (40.8° , 47.3° , and 69.6°) are



Fig. 5. SEM images of Pd-Co-10 (as-deposited): top-view (a-c), cross-sectional view (d). The insets show the images of Pd-Co-10 after electrochemical measurements. The arrow in "d" refers to the Pd-Co deposit on the Au substrate.

similar to those of the fcc Pd, except for slight shifts to higher angles. Those shifts indicate that the Pd lattice was contracted by replacing fcc Pd atoms with Co atoms [41], thus, our Pd-Co were found to be substitutional solid solutions. These solid solutions are considered as stable in acid media according to previous reports (some ordered phases, e.g. $L1_0$ and $L1_2$, were reported to dissolve in acid) [42–44].

In addition, compositions in the crystalline parts of Pd-Co-10 and Pd-Co-200 are calculated as $Pd_{87}Co_{13}$ and $Pd_{82}Co_{18}$, respectively, on the basis of Vegard's rule using the angles of (1 1 1). These compositions are different from the bulk compositions by ICP-AES, thus, we speculate that our Pd-Co possibly contains amorphous parts, small crystals, and/or anisotropic crystals [45].

3.2.3. Morphology

SEM images of Pd-Co-10 before electrochemical measurements are shown in Fig. 5. To investigate influence of electrochemical measurements, images after electrochemical measurements are shown in the insets. Surface of Pd-Co-10 is smooth, and the thickness is uniform (ca. 190 nm). The influence of electrochemical measurements is only increase of particle size to ca. 10 nm (Fig. 5c), while obvious changes are not observed in the macroscopic structure (Fig. 5a, b and d). Thus, we confirm Pd-Co is stable to some extent even in acid media.

SEM images of Pd-Co-200 after electrochemical measurements are shown in Fig. 6. Macroscopically, Pd-Co-200 is rough, and the deposits are dendritic, hence we confirm that porous Pd-Co films were successfully prepared by applying high current density. Particle size is larger (ca. 50 nm) than that of Pd-Co-10 (ca. 10 nm).

3.3. Electrochemical response

CV of Pd-Co-10 is compared with that of Pd-Co-200 and that of Pd in Fig. 7a. The CVs show redox responses in two potential regions: hydrogen region (-0.2 to 0.1 V) and oxide region (0.4-1.0 V). The CVs of Pd-Co is similar to that of Pd, while some sharp peaks are observed in the hydrogen region. The peaks of Pd-Co are similar to those of a Pd-black reported by Chevillot et al. [46], thus we identify the peaks of Pd-Co according to the peaks of Pd-black as follows:

• Peak 1 (0.05 V): Hydrogen adsorption/desorption (strongly bound) for surface Pd.



Fig. 6. SEM images of Pd-Co-200 deposited after electrochemical measurements: top-view (a-c), cross-sectional view (d).



Fig. 7. CVs of Pd-Co-10 (black line), Pd-Co-200 (grey line), and Pd (dotted line) in 0.5 mol dm⁻³ H₂SO₄: current density based on geometrical area (a), electrochemically active area (b). The insets indicate that oxide formation/deformation of Pd-Co occurs at lower potential than Pd. Sweep rate was 50 mV s⁻¹.

- Peak 2 (-0.05 V): Hydrogen absorption/desorption for inside Pd (α and β phases).
- Peak 3 (-0.2 V): Hydrogen adsorption/desorption (lessstrongly bound) for surface Pd.

Sharp peaks of Pd-Co (Peaks 1 and 3) are found to be attributed to the response from surface Pd, or Pd-skin.

To discuss quantitatively, CVs based on electrochemically active area (A_{ec}) are shown in Fig. 7b. A_{ec} was estimated using double layer capacitance (C_{dl}), assuming that values of C_{dl} per A_{ec} of different electrodes are the same. The value of C_{dl} per A_{ec} was calculated at $8.6 \times 10^{-2} \text{ mF cm}^{-2}$ using a flat Pt electrode according to the integral double layer capacitance ($3.1 \times 10^{-1} \text{ mF}, 0.2-0.25 \text{ V}$) and A_{ec} (15.5 cm^2) calculated according to hydrogen desorption charge [47]. According to the C_{dl} values, A_{ec} of Pd-Co-10, Pd-Co-200, and Pd were calculated at 1.5 cm^2 (0.13 mF), 6.1 cm^2 (0.52 mF), and 0.4 cm^2 (0.034 mF), respectively. Here we find that the larger response of Pd-Co-200 compared with Pd-Co-10 in Fig. 7a is attributed mainly to the increase of surface area because the CVs in Fig. 7b appears to be almost the same.

Electrochemical response of Pd-Co electrode is compared with that of Pd using the CVs based on A_{ec} (Fig. 7b) to clarify the alloying effect. In the hydrogen region, current densities of Pd-Co alloys are smaller than that of Pd. Peak 2, that is hydrogen absorption into Pd-Co, is obviously smaller than that of Pd. The results indicate that alloying with Co prevents hydrogen absorption into Pd-Co. In the oxide region, current densities of Pd-Co are almost the same as that of Pd, while the potential of oxide formation/deformation of Pd-Co was shifted to lower potential. Thus, the Pd-skin of Pd-Co is found to be easily oxidized compared with pure Pd. This result is different from higher potential shift reported on Pt alloys [48,49].

3.4. Catalytic activity

3.4.1. Oxygen reduction activity

LSV of oxygen reduction on Pd-Co-10 and the corresponding Tafel plots based on A_{ec} are compared with that of Pt and that of Pd in Fig. 8. By comparison of Pd-Co-10 and Pd-Co-200 in Fig. 8a, current of Pd-Co-200 near onset potential (~0.7 V) is significantly larger than that of Pd-Co-10 as expected from the larger surface area. The specific activity of Pd-Co-200 and Pd-



Fig. 8. Oxygen reduction activity of Pd-Co compared with Pt and Pd. (a) LSVs of oxygen reduction on Pd-Co-10 (black line), Pd-Co-200 (grey line), Pt (dashed line), and Pd (dotted line). Sweep rate was 1 mV s^{-1} . (b) Tafel plots based on electrochemically active area on Pd-Co-10, Pd-Co-200 (deposited for 5 s to obtain linear behavior [32]), Pt, and Pd.

Co-10 is almost the same as shown in Fig. 8b. By comparison of Pd-Co and Pt, the limiting current densities (ca. -0.4 mA cm^{-2} , Fig. 8a) and the potential gradients (ca. 60 mV dec.⁻¹, Fig. 8b) are almost the same, thus, oxygen reduction of our Pd-Co films probably follows the similar mechanism to Pt as reported by Ota et al. [18,50]. Potentials at low current density, $1.0 \,\mu\text{A cm}^{-2}$ (A_{ec}), are 0.68 V for Pd-Co, 0.73 V for Pt, and 0.58 V for Pd (Fig. 8b). Oxygen reduction activity of Pd-Co was confirmed to be higher than Pd and lower than Pt. The increase of catalytic activity of our Pd-Co compared with Pd is partly attributed to the electronic effect; because Pd–O bond of the Pd-skin should be more stable than Pd as mentioned above. Moreover, geometric effect possibly contributes to the increase as reported on the Pt-alloy systems [48,49].

3.4.2. Methanol tolerance

LSV of oxygen reduction in the presence of 1 mol dm^{-3} methanol on Pd-Co-10 and that on Pd-Co-200 are compared with that on Pt and that on Pd in Fig. 9a. Potentials at $1.0 \,\mu\text{A cm}^{-2}$ (A_{ec}) are 0.62 V for Pd-Co-10, 0.66 V for Pd-Co-200, 0.27 V for Pt, and 0.51 V for Pd. These values are compared with those in the absence of methanol in Fig. 9b. From the comparison, significantly high methanol tolerance of our Pd-Co films compared with Pt is clearly confirmed. The slight decrease of



Fig. 9. Methanol tolerance of Pd-Co compared with Pt and Pd during oxygen reduction in the presence of 1 mol dm⁻³ methanol. (a) LSVs for Pd-Co-10 (black line), Pd-Co-200 (grey line), Pt (dashed line), and Pd (dotted line). Sweep rate was 1 mV s⁻¹. (b) Comparison of the potentials of oxygen reduction at 1 μ A cm⁻² (A_{ec}) in the condition w/o or w/methanol.



Fig. 10. Cell performance of a micro-DMFC with different cathode catalyst: (a) Pt and (b) Pd-Co catalyst. Fuel solution: $1 \text{ mol } dm^{-3}$ methanol solution containing 0.5 mol dm⁻³ sulfuric acid. Oxidant solution: oxygen saturated 0.5 mol dm⁻³ sulfuric acid w/o or w/1 mol dm⁻³ methanol. Flow rate: $80 \,\mu L \,min^{-1}$. Temperature: room temperature.

potential caused by addition of methanol is probably attributed to methanol adsorption on the surface as reported by Ota and co-workers [18].

As for activity during fuel cell operation, current–voltage (current–power) curves in the presence or the absence of methanol are shown in Fig. 10. In the case of Pt cathode (Fig. 10a), the voltage significantly decreases by adding 1 mol dm^{-3} methanol to the cathode channel, e.g. open circuit voltage decreases from 0.55 to 0.19 V. However, in the case of Pt-Co cathode (Fig. 10b), the current–voltage curve does not show any remarkable changes even in the presence of methanol, thus we confirmed the excellent methanol tolerance of our Pd-Co during fuel cell operation.

4. Conclusions

Electrodeposited Pd-Co was found to be a solid solution of ca. Pd_7Co_3 with Pd-skin. As for catalytic activity in oxygen reduction, the Pd-Co possessed comparable activity to Pt (potential difference at 1.0 μ A cm⁻² (A_{ec}) was 0.05 V). Moreover, the Pd-Co possessed significantly higher methanol tolerance than Pt.

Furthermore, we obtained different morphology (smooth or dendritic) with almost the same structures and catalytic activ-

ity. Thus, we conclude that electrodeposition is applicable for preparing Pd-Co alloy as ORR catalyst for fuel cells. Our approach will extend application of Pd-Co catalyst to porous metal electrodes.

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References

- H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Appl. Catal. B: Environ. 56 (2005) 9.
- [2] H. Liu, C. Song, L. Zhang, J. Zhang, H. Wang, D.P. Wilkinson, J. Power Sources 155 (2006) 95.
- [3] J.L. Fernández, V. Raghuveer, A. Manthiram, A.J. Bard, J. Am. Chem. Soc. 127 (2005) 13100.
- [4] R. Bashyam, P. Zelenay, Nature 443 (2006) 63.
- [5] P. Convert, C. Coutanceau, P. Crouigneau, F. Gloaguen, C. Lamy, J. Appl. Electrochem. 31 (2001) 945.
- [6] T.J. Shcmidt, U.A. Paulus, H.A. Gasteiger, N. Alonso-Vante, R.J. Behm, J. Electrochem. Soc. 147 (2000) 2620.
- [7] H. Tributsch, M. Bron, M. Hilgendorff, H. Schulenburg, I. Dorbandt, V. Eyert, P. Bogdanoff, S. Fiechter, J. Appl. Electrochem. 31 (2001) 739.
- [8] S.S. Kocha, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells, vol. 3, Wiley, England, 2003 (Chapter 43).
- [9] E.H. Yu, K. Scott, R.W. Reeve, L. Yang, R.G. Allen, Electrochim. Acta 49 (2004) 2443.
- [10] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, Electrochem. Commun. 6 (2004) 562.
- [11] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, Electrochemistry 73 (2005) 346.
- [12] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, Electrochemistry 73 (2005) 352.
- [13] S.C. Kelley, G.A. Deluga, W.H. Smyrl, Electrochem. Solid-State Lett. 3 (2000) 407.
- [14] J. Jiang, A. Kucernak, Chem. Mater. 16 (2004) 1362.
- [15] Y. Yamauchi, K. Kuroda, Electrochem. Commun. 8 (2006) 1677.
- [16] Y. Yamauchi, T. Ohsuna, K. Kuroda, Chem. Mater. 19 (2007) 1335.
- [17] O. Savadogo, K. Lee, K. Oishi, S. Mitsushima, N. Kamiya, K. Ota, Electrochem. Commun. 6 (2004) 105.

- [18] K. Lee, O. Savadogo, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, J. Electrochem. Soc. 153 (2006) A20.
- [19] V. Raghuveer, A. Manthiram, A.J. Bard, J. Phys. Chem. B 109 (2005) 22909.
- [20] J.L. Fernández, D.A. Walsh, A.J. Bard, J. Am. Chem. Soc. 127 (2005) 357.
- [21] W.E. Mustain, K. Kepler, J. Prakash, Electrochem. Commun. 8 (2006) 406.
- [22] W.E. Mustain, K. Kepler, J. Prakash, Electrochim. Acta 52 (2007) 2102.
- [23] Y. Wang, P.B. Balbuena, J. Phys. Chem. B 109 (2005) 18902.
- [24] M.H. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, M.B. Vukmirovic, R.R. Adzic, Langmuir 22 (2006) 10409.
- [25] L. Zhang, K. Lee, J. Zhang, Electrochim. Acta 52 (2007) 3088.
- [26] V. Raghuveer, P.J. Ferreira, A. Manthiram, Electrochem. Commun. 8 (2006) 807.
- [27] V.A. Paganin, E. Sitta, T. Iwasita, W. Vielstich, J. Appl. Eletrochem. 35 (2005) 1239.
- [28] B. Gurau, E.S. Smotkin, J. Power Sources 112 (2002) 339.
- [29] R.D. Noce, N. Barelli, P.T.A. Sumodjo, D.R. Cornejo, A.V. Benedetti, J. Magn. Magn. Mater. 306 (2006) 199.
- [30] R. Gontarz, L. Smardz, B. Szymanski, P. Juzikis, J. Magn. Magn. Mater. 120 (1993) 278.
- [31] J. A. Abys, I. Boguslavsky, H. K. Straschil, US Patent 5976344, Nov. 2, 1999.
- [32] S. Tominaka, S. Ohta, T. Momma, T. Osaka, ECS Trans. 11 (2007) 1369.
- [33] R.L. Penven, W. Levason, D. Pletcher, J. Appl. Electrochem. 20 (1990) 399.
- [34] M.R. Winchester, R. Payling, Spectrochim. Acta B 59 (2004) 607.
- [35] J. Pisonero, B. Fernández, R. Pereiro, N. Bordel, A.S. Medel, Trac-Trends Anal. Chem. 25 (2006) 11.
- [36] M.P. Seah, I.S. Gilmore, S.J. Spencer, J. Electron Spectrosc. Relat. Phenom. 120 (2001) 93.
- [37] T. Toda, H. Igarashi, M. Watanabe, J. Electrochem. Soc. 145 (1998) 4185.
- [38] T. Toda, H. Igarashi, M. Watanabe, J. Electroanal. Chem. 460 (1999) 258.
- [39] F.L. Williams, D. Nason, Surf. Sci. 45 (1974) 377.
- [40] L. Guczi, Z. Shay, G. Stefler, F. Mizukami, J. Mol. Catal. A: Chem. 141 (1999) 177.
- [41] V. Jalan, E.J. Taylor, J. Electrochem. Soc. 130 (1983) 2299.
- [42] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, A.K. Niessen, Cohesion in Metals: Transition Metal Alloys, vol. 1, North-Holland, New York, 1988.
- [43] Y. Matsuo, J. Phys. Soc. Jpn. 32 (1972) 972.
- [44] T. Mallát, J. Petró, J. Electroanal. Chem. 208 (1986) 169.
- [45] L.I. Kveglis, S.M. Jarkov, I.V. Saroverova, Phys. Solid State 43 (2001) 1543.
- [46] J.P. Chevillot, J. Farcy, C. Hinnen, A. Rousseau, J. Electroanal. Chem. 64 (1975) 39.
- [47] T. Biegler, D.A.J. Rand, R. Woods, J. Electroanal. Chem. 29 (1971) 269.
- [48] J.F. Drillet, A. Ee, J. Friedemann, R. Kötz, B. Schnyder, V.M. Schmidt, Electrochim. Acta 47 (2002) 1983.
- [49] R.K. Raman, G. Murgia, A.K. Shukla, J. Appl. Electrochem. 34 (2004) 1029.
- [50] E. Yeager, Electrochim. Acta 29 (1984) 1527.