



Short communication

Nanostructured catalyst with hierarchical porosity and large surface area for on-chip fuel cells

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ABSTRACT

This communication reports the synthesis of mesoporous Pd–Co dendrites with both a unique hierarchical porosity and a large surface area by the combination of electrodeposition and dealloying. The resultant mesoporous dendrites consist of microparticles with a diameter of a few hundred nanometers, and the particles have mesopores with around 10 nm width. The mesoporous dendrites are found to be Pd₅Co₂, to be composed of pure Pd crystalline phases and amorphous Pd–Co phases, and to be covered with Pd-skin layers. This catalyst exhibits a high activity in the oxygen reduction reaction. Thus, this novel catalyst is attractive as a catalyst for on-chip fuel cells, which require catalysts to be deposited precisely onto tiny current collectors.

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1. Introduction

Recent progress in micro-electrochemical devices, *e.g.*, on-chip fuel cells [1–4], micro-batteries [5,6], and on-chip sensors [7,8], inevitably requires developments of both electrode materials with a large surface area and processes for depositing such materials precisely onto their tiny current collectors. To increase electrode surface area of interest, nanostructured materials including nanoparticles and nanoporous films have been widely used, and are effective for the improvements of electrochemical devices. Moreover, each of the devices needs electrodes with a different porosity appropriate to its own requirements for reactant- and product-transportations. Thus, we have synthesized dendritic nanostructures, whose pores were expected to make the entire surface readily accessible by the reactants, as catalysts for on-chip fuel cells by means of electrodeposition, because this technique can deposit nanostructured materials precisely onto microelectrodes fabricated even in a confined space [9].

Electrodeposition is an important technique for synthesizing electrode materials for micro-electrochemical devices because of its direct synthesis of metal alloys without a thermal treatment and its selective deposition onto conductive materials [9–11]. Moreover, morphology of the deposits can be controlled with the applied current [11,12]. In view of this, we electrodeposited elec-

trode catalysts for on-chip fuel cells, *e.g.*, Pt black, Pt–Ru alloy and Pd–Co alloy [1,2,10,13], but their roughness factors, which are defined as ratios of the actual electrode surface area divided by the geometrical one, were one order of magnitude lower than those of the general fuel cell electrodes prepared from nanoparticles [4]. For instance, general direct methanol fuel cells require Pt loading of about 2.5 mg cm⁻², translating into a roughness factor of 2000 (80 m² g⁻¹), but such factor of our on-chip fuel cells has been limited to less than 100 due to space limitation. This large gap is because the particles of the electrodeposited dendrites were more than 10 times as big as the nanoparticles generally used for fuel cells. In order to increase the surface area of such electrodeposits, deposition with a template has been widely used [14–19], however, such a template process seems complicated and lead to increase in process steps. Therefore, we consider that more versatile methods for synthesizing nanostructured electrodes for micro-electrochemical devices need to be developed.

In order to prepare electrode materials with a large surface area, we focus on dealloying technique, which refers to the selective dissolution of one or more components out of an alloy; because this technique has been widely applied to synthesize sponge-like porous materials of, *e.g.*, Pt, Au and Cu, without any template [20–23]. The unique porous structure is formed by a competition of two processes: dissolution of less-noble component (*i.e.*, pore formation) and surface diffusion of more noble component to aggregate into two-dimensional clusters (*i.e.*, surface passivation) [24–28]. Their surface area can reach a value comparable to those of nanoparticles when the pore size gets to a mesoscale [29]; however,

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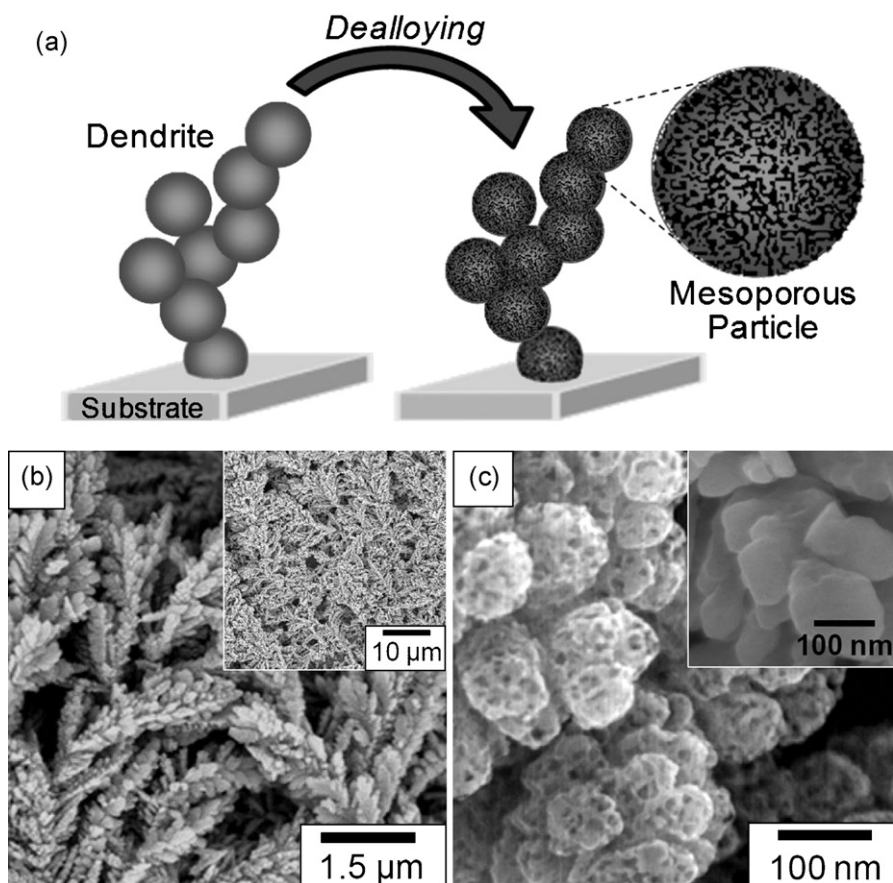


Fig. 1. (a) Schematic illustration representing the synthesis of mesoporous Pd–Co dendrites. (b and c) Plan-view scanning electron micrographs of Pd–Co dendrites electrodeposited at a constant current of -50 mA cm^{-2} for 600 s after dealloying by the immersion in an air-saturated 0.5 M sulfuric acid solution for $\sim 15 \text{ h}$ at 60°C . The inset in (b) shows a low-magnification image. The inset in (c) shows an image of the dendrites before the dealloying process.

for use as an electrode for fuel cells, mass-transfers seem hampered by their small and tortuous pores. On this point, we conceived that the macropores between dendrites formed by electrodeposition can compensate for the limitation.

Here we propose a simple method to synthesize a unique nanostructure with both a hierarchical porosity and a large surface area, *i.e.*, mesoporous dendrites, which have macropores between dendrites formed by electrodeposition and mesopores formed by dealloying (Fig. 1a). In addition to the unique structure, we emphasize that this material can be added even onto tiny current collectors for micro-electrochemical devices. To demonstrate this idea, mesoporous Pd–Co dendrites were synthesized as catalyst for on-chip fuel cells by the combination of electrodeposition and dealloying. Since Pd-based catalysts (*e.g.*, $\text{Pd}_x\text{Co}_{1-x}$, $x = 0.6\text{--}0.8$) are both highly active in the oxygen reduction reaction and highly tolerant to the presence of methanol [30–35], we have used this catalyst for realizing a tiny on-chip direct methanol fuel cell of a membraneless design [1]. To obtain such an active Pd–Co catalyst with a hierarchical porosity, first, a Co-rich alloy was electrodeposited as dendrites, and then the dendrites were partially dealloyed by the immersion in a sulfuric acid solution to become a Pd-rich alloy.

2. Experimental

Pd–Co was electrodeposited by applying a galvanic pulse (on: -40 mA cm^{-2} for 1 s; off: 2 s; 500 cycles) in a solution containing 34 mM $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, 76 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 120 mM malonic acid and 76 mM NH_4Cl (pH 10, adjusted by NH_4OH) at room tempera-

ture. The cell was a conventional three-electrode cell with a 200 nm thick Au substrate (the working electrode), which was prepared by electron-beam deposition on a Si substrate with a Ti adhesion layer [10], a Pt wire counter electrode and a Ag/AgCl/KCl (saturated) reference electrode. The electrodeposits were dealloyed by immersing in an air-saturated 0.5 M H_2SO_4 at 60°C overnight ($\sim 15 \text{ h}$). This dealloyed catalyst was cleaned by scanning in a nitrogen-saturated 0.5 M sulfuric acid solution at 30°C in the potential range of 1.0–0.2 V vs. Ag/AgCl at 50 mV s^{-1} (60 cycles).

The electrochemical response from the dealloyed sample was evaluated by cyclic voltammetry (CV) in a nitrogen-saturated 0.5 M sulfuric acid solution (30°C) in the potential range of -0.2 to $+1.0 \text{ V}$ vs. Ag/AgCl at 50 mV s^{-1} . The roughness factor was calculated based on the double layer capacitance in the CVs (8.6 mF cm^{-2}) by following a previously published method [10]. The activity for the oxygen reduction reaction was evaluated by linear sweep voltammetry (LSV) in an oxygen-saturated 0.5 M sulfuric acid solution (30°C) from the open circuit potential to 0.6 V at 0.1 mV s^{-1} . The microscopic morphology was observed using a high-resolution scanning electron microscope (HR-SEM) (S-5500, Hitachi). The composition was determined by energy dispersive X-ray fluorescence spectroscopy (ED-XRF) ($\mu\text{EDX-1200}$, Shimadzu) from the Pd-K α peak at 21.12 keV and the Co-K α peak at 6.92 keV using a Rh target (50 kV). The surface composition and the surface elemental state were evaluated by X-ray photoelectron spectroscopy (XPS) (ESCA1800MC, ULVAC-PHI) using a Mg target (standard) at 14 kV, 400 W. The crystal structure was examined by means of X-ray diffractometry (XRD) using a Cu-K α radiation at 40 kV (40 mA), with a two-dimensional detector (D8 Discover with GADDS, Bruker).

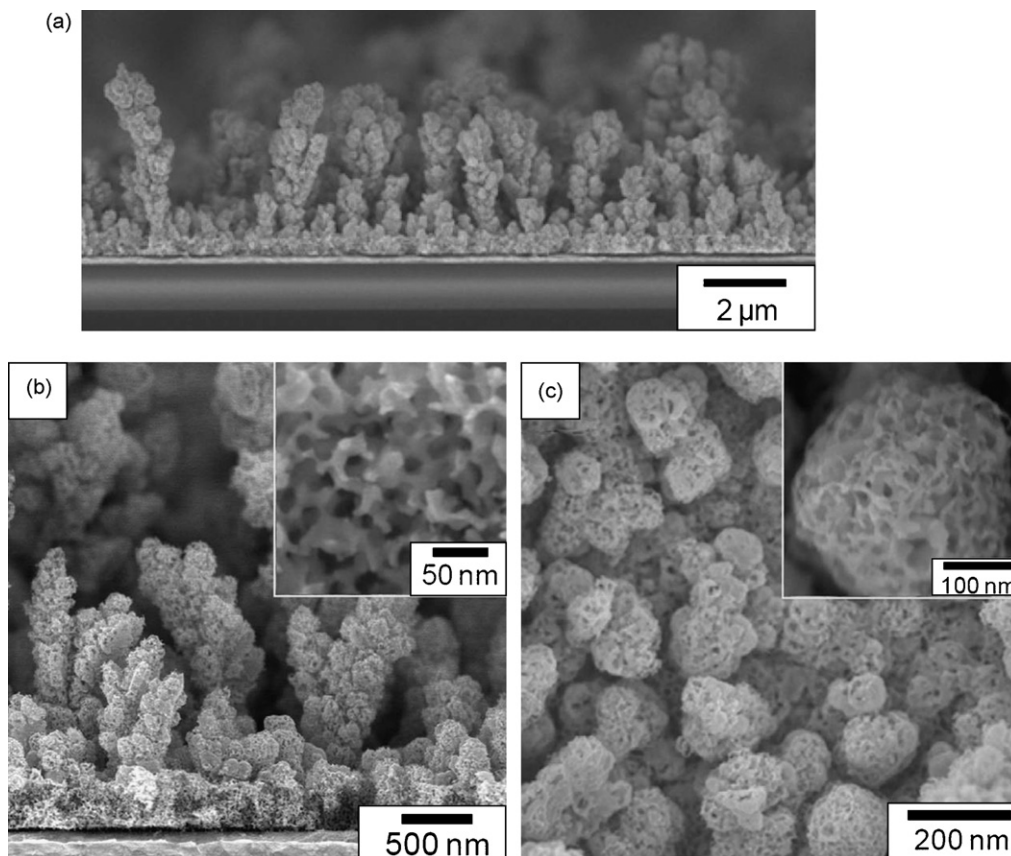


Fig. 2. High-resolution scanning electron micrographs of mesoporous Pd–Co dendrites prepared by galvanic pulse deposition (after dealloying). (a and b) Cross-sectional images. (c) Plan-view image. The insets show magnified images.

3. Results and discussion

First of all, we demonstrated the concept by depositing a Pd–Co alloy simply at a constant current. The resultant electrodeposits were in a form of mesoporous dendrites as shown in the SEM images (Fig. 1b and c). Compared with as-deposited ones, the mesopores were found to be formed without changing the macroscopic morphology of dendrites (Fig. 1c). These deposits seemed to be too thick to use as a catalyst for on-chip fuel cells, the deposition conditions were adjusted by applying a pulse current. The resultant electrodeposits were also in a form of mesoporous dendrites as shown in the SEM images (Fig. 2a–c). The deposited layer was thin enough (4–5 μm) for use as a catalyst for on-chip fuel cells, and was composed of dendrites, which are typical for electrodeposits prepared by applying a large current density. The macropores between the deposits are expected to make the entire surface of the dendrites readily accessible by the reactants of the fuel cell reaction, *i.e.*, the oxygen reduction reaction. The dendrites consisted of microparticles with a diameter of a few hundred nanometers, and the particles had mesopores with around 10 nm width. The sponge-like porous structure is typical for the metal architecture prepared by dealloying. One may wonder if the dealloyed dendrites had any Co atoms left, thus this new material was characterized as follows.

The deposits were characterized by using XRF, XRD and XPS. The XRF results indicate that the bulk composition of the dealloyed Pd–Co deposits was still an alloy, *i.e.*, Pd₇₉Co₂₁. Compared with the composition of the as-deposited ones (*i.e.*, Pd₂₄Co₇₆), about 90% of Co atoms was leached out during the dealloying process, this in turn translating into the porosity of 67% as calculated using atomic radius (Pd: 1.37 Å, and Co: 1.25 Å). The XRD results

(Fig. 3A) indicate that the crystal structure of the sample was drastically changed from amorphous to crystalline. In detail, the XRD pattern of the as-deposited Pd–Co alloy was peak-less, except for the sharp peaks attributed to the Au substrate and a small peak around 42° which is assigned to hcp-Co (1 0 0) (41.6° from JCPDS data No. 89-4308), which meant that the as-deposited alloy was amorphous in X-ray. This amorphous structure was changed by dealloying to a crystalline pure Pd phase, judging from the diffraction angles of the sharp peaks (40.0° and 46.3°) consistent with those of a pure fcc-Pd lattice (40.0° for (1 1 1) and 46.5° for (2 0 0), from JCPDS data No. 88-2335). These results indicate that the mesoporous dendrites contained both crystalline pure Pd phases and amorphous Pd–Co phases. This is probably because Pd–Co alloy systems contained some ordered phases with different acid stabilities, whose crystallites were reported too small to be detected by X-ray [36,37].

The surface composition was determined to be nearly pure Pd from the XPS results (Fig. 3B), indicating that the surface was covered with a Pd-skin layer. This Pd skin was probably in the metallic state, judging from the Pd 3d_{5/2} peak energy which is consistent with that of a metallic Pd (Fig. 3B). Such a Pd-skin layer is typical for acid-treated alloys of a noble metal and a transition metal [38,39]. This layer probably protected the residual Co atoms in the subsurface alloy phases from leaching out, but there is still a possibility that the Co atoms were heterogeneously distributed in the deposits. As we described above, Pd atoms in some easily dissolvable phases, *e.g.*, solid solutions and intermetallic compounds of PdCo₃ (L₁₂ phase) [37], probably resulted in thick Pd-skin layers that incorporated some relatively stable phases, *e.g.*, Pd₃Co (L₁₂ phase) and PdCo (L₁₀ phase). Thus, we'll use transmission electron microscopy to conclude this point.

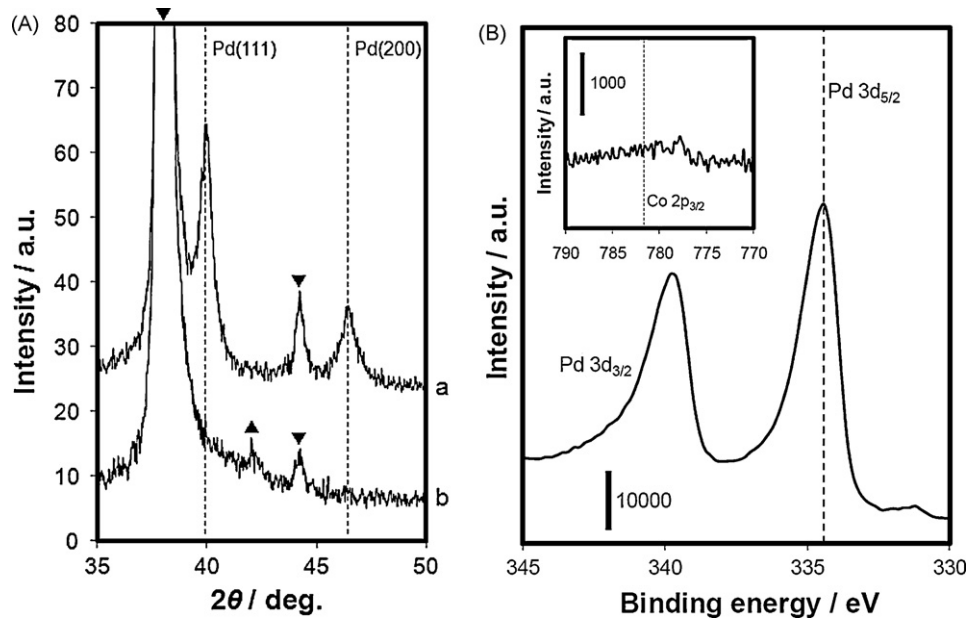


Fig. 3. Characteristics of mesoporous Pd–Co dendrites. (A) X-ray diffraction patterns of (a) mesoporous Pd–Co and (b) as-deposited Pd–Co. ▼: Au substrate. ▲: hcp-Co. (B) X-ray photoelectron spectra of Pd and Co (inset).

The CVs in an inert solution (Fig. 4a) show that the CV trace of the mesoporous Pd–Co catalyst was typical for a Pd–Co alloy [9], in view of (i) the sharp redox peaks attributed to the hydrogen adsorption–desorption reactions in the range of -0.2 to $+0.2$ V (see the inset of Fig. 4a), (ii) the oxidation current associated with the formation of surface oxide from 0.5 to 1.0 V, and (iii) the reduction current associated with the deformation of surface oxide from 0.8 to 0.4 V. As we discussed in a paper previously published [10], the sharp peaks in the hydrogen region probably originate from the formation of a Pd-skin layer. The peak potential of the oxide deformation current at *ca.* 0.55 V was more negative than that of a pure Pd (*i.e.*, 0.56 V) [10], this indicating that the Pd-skin layer was prone to be bonded to oxygen species compared with a bulk Pd. Although the potential was higher than that of the conventional Pd–Co dendrites

(*i.e.*, 0.53 V) [13], we still expected a favorable catalytic activity of this catalyst.

Next, we compared the electrochemical characteristics with those of the conventional Pd–Co dendrites which we have used for the on-chip fuel cell [1,10]. The CVs (Fig. 4a) show that the electrochemical response from the mesoporous dendrites was significantly larger than that of the conventional Pd–Co dendrites without mesopores. The roughness factor of the mesoporous one was determined to be *ca.* 290 by the calculation using the double layer capacitance at 0.4 V [10]. This value is more than 20-fold of the value of the conventional Pd–Co catalyst without mesopores (*ca.* 13) [13], indicating a positive effect of the formation of mesopores even though the mesoporous one is a few times thicker than the conventional one (*ca.* 1.5 μm). This quite

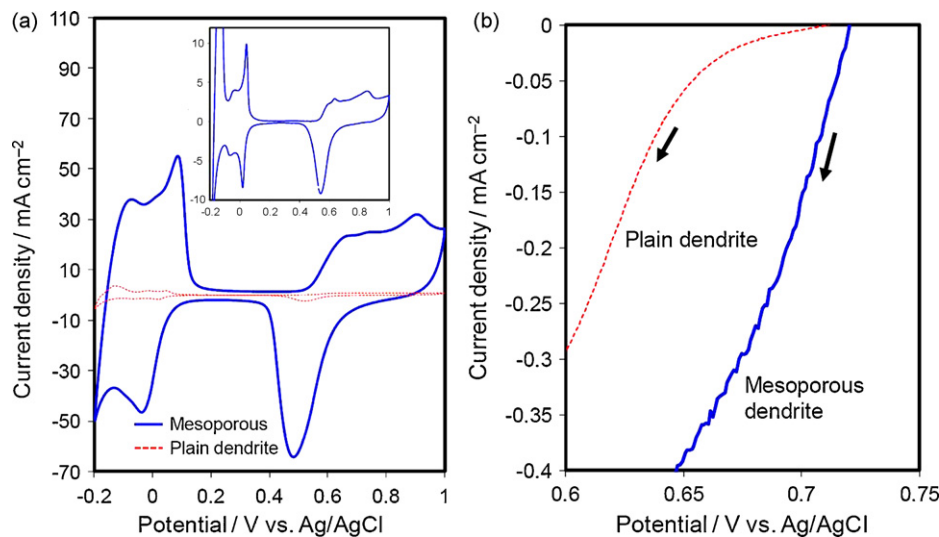


Fig. 4. Electrochemical properties of the mesoporous Pd–Co dendrites (solid line) compared with that of the conventional Pd–Co dendrites without pores (dotted line). (a) Cyclic voltammograms at 50 mV s^{-1} in a nitrogen-saturated 0.5 M H_2SO_4 solution at 30°C . The inset shows a low scan-rate voltammogram at 5 mV s^{-1} . (b) Linear sweep voltammograms for the oxygen reduction reaction in an oxygen-saturated 0.5 M H_2SO_4 solution at 30°C . Scan rate: 0.1 mV s^{-1} for the mesoporous dendrites, 1 mV s^{-1} for the simple dendrites. The lower scan rate for the evaluation of the mesoporous one was chosen to reduce the influence of oxide reduction current on the oxygen reduction current.

large surface area is expected to improve the electrode performance.

The oxygen reduction reaction activity was evaluated by LSV in an oxygen-saturated solution (Fig. 4b). The onset potential was *ca.* 0.72 V vs. Ag/AgCl, which was equal to that of the conventional one without mesopores. The current density was *ca.* $-160 \mu\text{A cm}^{-2}$ at 0.7 V, *i.e.*, about 40-fold of that of the conventional one (*ca.* $-4.3 \mu\text{A cm}^{-2}$), indicating that the increase in the roughness factor was effective for the improvement of electrode performance and moreover that the specific activity was probably superior to that of the conventional one. This performance improvement in turn resulted in the potential increase as large as *ca.* 70 mV (at -0.1 mA cm^{-2}) compared with that of the conventional dendrites. These results strongly indicate that this mesoporous Pd–Co dendrites will be effective for the performance improvement of on-chip fuel cells.

4. Conclusion

In summary, mesoporous Pd–Co dendrites with both a unique hierarchical porosity and a large surface area were successfully synthesized by the combination of electrodeposition and dealloying. The mesoporous catalyst exhibited a high activity in the oxygen reduction reaction. It is concluded that this mesoporous Pd–Co alloy is a promising candidate for the catalyst of on-chip fuel cells.

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