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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 Pd_8Co_2, 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.

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 electrocatalysts 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 ($80\,m^2\,g^{-1}$), 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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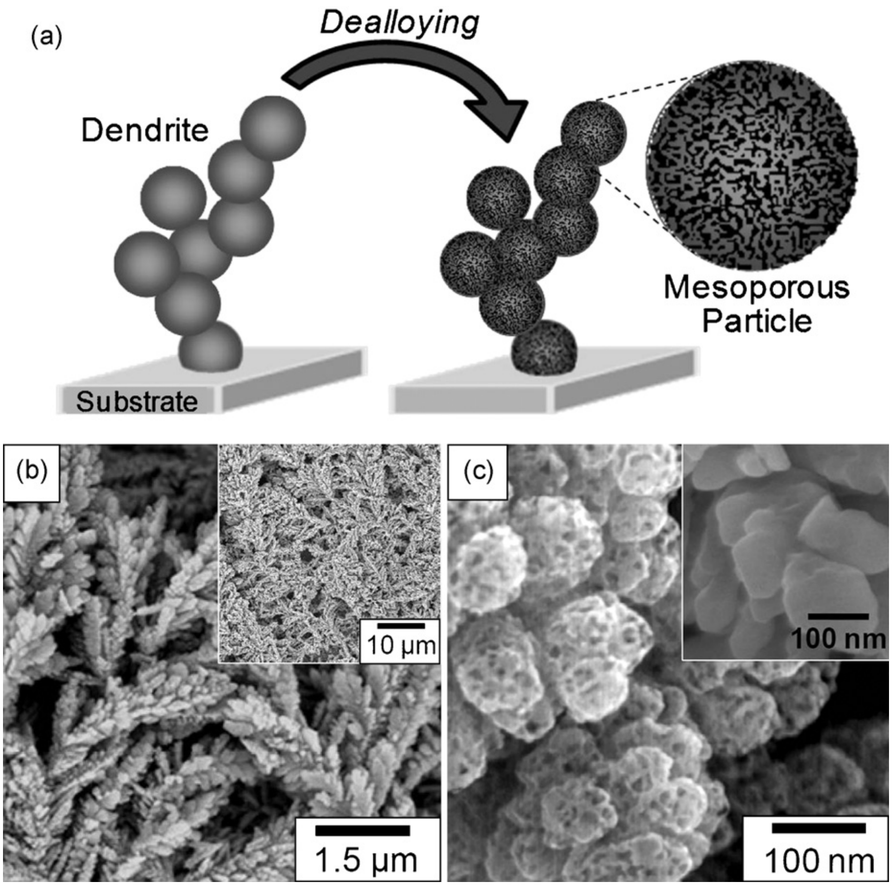

Fig. 1. (a) Schematic illustration representing the synthesis of mesoporous Pd–Co dendrites. (b and c) Plan-view scanning electron micrographs of Pd–Co dendrites electrodeposited at a constant current of $-50\,\mathrm{mA\,cm^{-2}}$ for 600 s after dealloying by the immersion in an air-saturated 0.5 M sulfuric acid solution for ~15 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.*, Pd_xCo_{1-x}, $x = 0.6$–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: $-40\,\mathrm{mA\,cm^{-2}}$ for 1 s; off: 2 s; 500 cycles) in a solution containing 34 mM $[Pd(NH_3)_4]Cl_2$, 76 mM $CoCl_2{\cdot}6H_2O$, 120 mM malonic acid and 76 mM NH_4Cl (pH 10, adjusted by NH_4OH) at room temperature. 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 (~15 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 $50\,\mathrm{mV\,s^{-1}}$ (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 V *vs.* Ag/AgCl at $50\,\mathrm{mV\,s^{-1}}$. The roughness factor was calculated based on the double layer capacitance in the CVs ($8.6\,\mathrm{mF\,cm^{-2}}$) 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 $0.1\,\mathrm{mV\,s^{-1}}$. 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) (μEDX-1200, Shimadzu) from the Pd-Kα peak at 21.12 keV and the Co-Kα 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-Kα radiation at 40 kV (40 mA), with a two-dimensional detector (D8 Discover with GADDS, Bruker).