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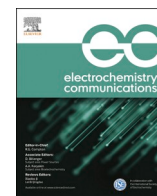
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Modification with platinum of silver-deposited nickel wire electrodes for electrocatalytic oxidation of alcohols

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ABSTRACT

A silver-deposited nickel (Ag/Ni) wire electrode was prepared via a galvanic replacement reaction between Ag⁺ and Ni wire in aqueous solution. It was then found that the Ag/Ni wire electrode could be modified with Pt simply by treating it in an aqueous solution of K₂PtCl₄. Although the deposition of Ag on Ni wire was limited in amount, forming Ag deposits less than 100 nm in size, a considerable increase in the electrocatalytic currents for the oxidation of alcohols could be observed after further modification of the Ag/Ni wire electrodes with Pt. This is in contrast to the fact that it was difficult to produce sufficient electrocatalytic response by modifying Ni wire with Pt directly via a simple galvanic replacement between PtCl₄²⁻ and Ni wire. Thus, the prior deposition of Ag was found to strongly promote modification with Pt via a simple stepwise treatment using AgNO₃ and K₂PtCl₄. This approach should be effective in modifying various Ni materials with Pt, including Ni microparticles.

1. Introduction

Direct alcohol fuel cells have attracted much attention in recent years, as summarized in several reviews [1–4]. While Pd-based [1] or Pt-free [2] electrocatalysts have been developed for oxidation of alcohols, Pt-based electrocatalysts are still the main focus for the oxidation of alcohols in acidic and alkaline media [3,4]. Recently some attention has also been paid to noble-metal-based binary or ternary nano-electrocatalysts [3,4].

We are interested in the modification or deposition of noble metals, such as Au and Pd, via galvanic replacement reactions, and have reported several results over recent years [5–9]. Modification with Au is possible on Ni [5] and Ti [9] wire electrodes, with applicability to electroanalysis. The deposition of Pd is possible on Ni wires [6], including co-deposition of Pd with Au [8] and Ni microparticles [7]. Ni materials deposited with Pd should be effective for the electrocatalytic oxidation of ethanol in alkaline solutions [6–8]. However, we could not report the electrochemical properties of Ni materials deposited with Pt due to the difficulty in depositing Pt on Ni in the same manner, i.e., simply immersing Ni materials in aqueous solutions of K₂PtCl₄ or K₂PtCl₆. In our previous work on Pd deposition on Ni wire [6], Pt deposition on Ni wire was also examined, but it was found and reported

that deposition of Pt on Ni wire was much poorer than that of Pd.

In the present work, we have found that Pt deposition was promoted on Ag-deposited Ni (Ag/Ni) wire electrodes. First, the deposition of Ag was explored via galvanic replacement between Ag⁺ and Ni wire by immersing the Ni wire in aqueous solutions of AgNO₃. Then, the resulting Ag/Ni wire electrodes were treated in aqueous solutions of K₂PtCl₄ for modification with Pt. Finally, we evaluated the electrocatalytic properties of the Pt-modified Ag/Ni wire electrodes by observing the electrochemical responses of alcohols in alkaline solutions.

Among Pt-based binary nanocatalysts, the combination of Ag and Pt would not rank very highly [3]. However, there are several reports of Ag-Pt binary electrocatalysts, i.e., Pt/C catalysts with Ag [10], AgPt aerogels [11], Ag@Pt nanorods on electrochemically reduced graphene oxide nanosheets [12], 3D porous PtAg nanotubes [13], and Pt₃Ag alloy wavy nanowires [14]. While nanostructuring has been reported for Ag-Pt electrocatalysts [10–14], we examined the modification with Pt mainly expecting simple galvanic replacement reactions between Ag and the Pt precursor ions [15–17]. Such galvanic replacement reactions have generally been focused on preparing electrocatalysts [18]. In combination with base Ni, a cascade galvanic replacement method for preparing PdAg/Ni foam has been reported [19]. While the approach is

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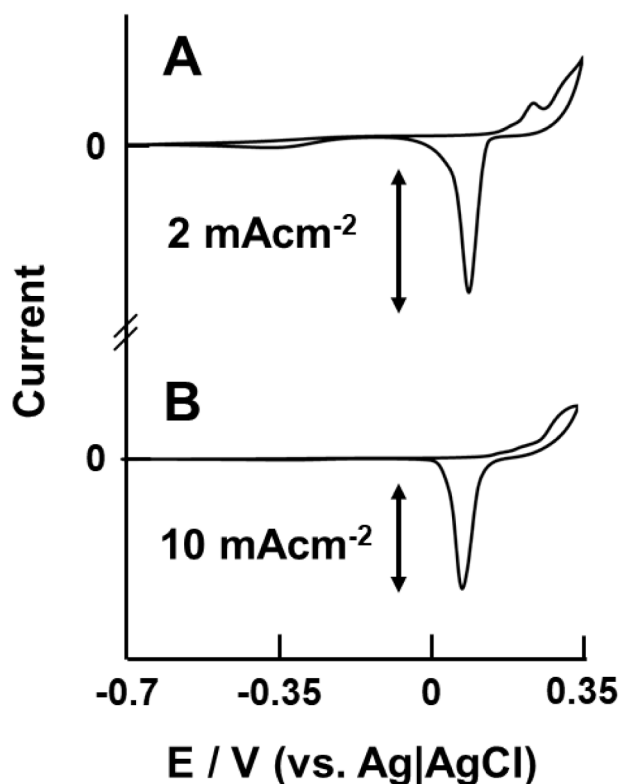


Fig. 1. Cyclic voltammograms recorded in 1.0 M NaOH aqueous solution with (A) a Ni wire electrode deposited with Ag using 1.0 mM AgNO_3 with an immersion time of 10 min, and (B) a Ag disk electrode. Scan rate: 50 mV/s.

similar to that reported for PdAg/Ni foam [19], the present work aims to explore the modification of Ni wire with Pt with the aid of pre-deposited Ag.

2. Experimental

Scanning electron microscope (SEM) images were obtained with a field emission SEM (FE-SEM) instrument (MERLINTM, Carl Zeiss Microscopy). Cyclic voltammograms (CVs) were recorded using a potentiostat (PGSTAT 128N, Metrohm Autolab). Platinum wire and a Ag|AgCl (3.0 M NaCl) electrode (BAS Inc.) were employed as the counter and reference electrodes, respectively. Ni wire (diam. 0.30 mm, 99+% degree, Nilaco Co.) was used to prepare the modified Ni electrodes. For purposes of comparison, a Pt disk (diam. 1.6 mm, BAS Inc.) and a Ag disk (diam. 1.6 mm, BAS Inc.) were also tested as working electrodes. K_2PtCl_4 , K_2PtCl_6 and AgNO_3 were purchased from Sigma-Aldrich. Other reagents were obtained from Sigma-Aldrich and Wako Pure Chemicals. All aqueous solutions were prepared with ultra-pure water obtained from a water purification system (arium® pro, Sartorius) with a specific resistance $>18 \text{ M}\Omega \text{ cm}$.

Before modification with Pt or Ag, a piece of Ni wire (diam. 0.30 mm, ca. 7 cm length) was washed with acetone and sonicated for 10 min, followed by a further 10 min sonication in 1.0 M HCl aqueous solution [6]. The washed Ni wire was then immersed in an aqueous solution of the precursor ions: AgNO_3 for Ag, and K_2PtCl_4 for Pt. The concentrations of AgNO_3 and K_2PtCl_4 were varied in the range 0.10–1.0 mM. Although K_2PtCl_6 was examined for the deposition of Pt, the results were not very different from those obtained with K_2PtCl_4 . All the treatments were carried out using 10 ml glass bottles. The temperature was kept at 30 °C using a thermostatic bath.

For electrochemical evaluation, 10 mm of the modified Ni wire working electrode was exposed to the electrolyte while the rest was covered by waterproof tape, and CVs of alcohols were recorded in

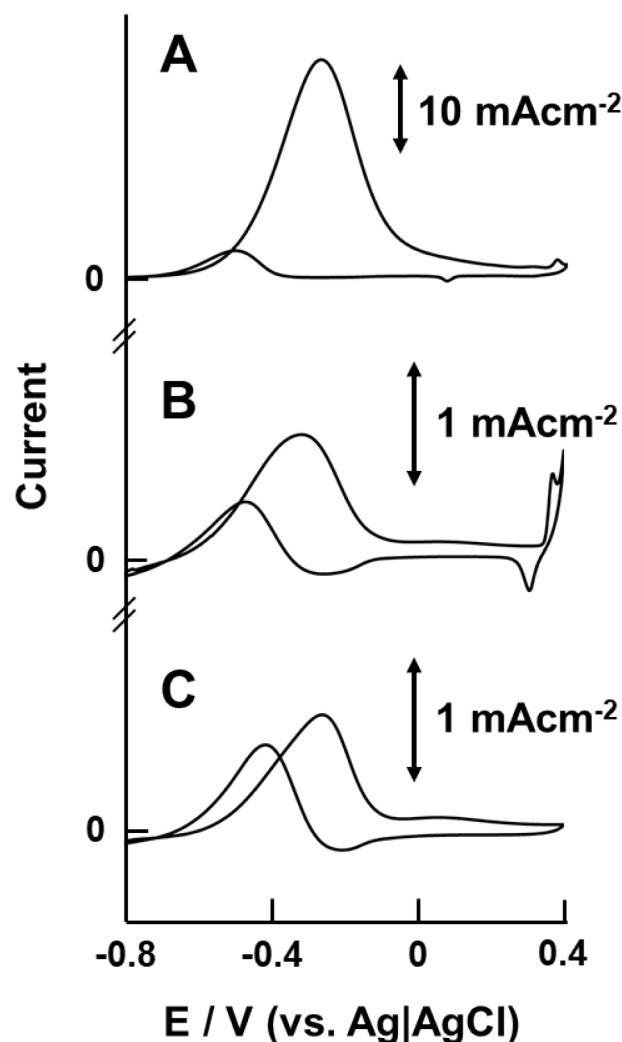


Fig. 2. Cyclic voltammograms of 1.0 M ethanol in 1.0 M NaOH aqueous solution recorded with (A) a Ag/Ni wire electrode modified with Pt by treating the Ag/Ni wire electrode of Fig. 1A in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min, (B) a Ni wire electrode deposited with Pt by immersing a piece of Ni wire in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min, and (C) a Pt disk electrode. Scan rate: 50 mV/s. The CVs of the 10th scan are shown.

alkaline solutions. To evaluate the current magnitude, the current value of the CVs was divided by the geometrical surface area of the 10 mm Ni cylinder (0.30 mm diameter) for the modified Ni wire electrodes.

3. Results and discussion

3.1. Deposition of Ag on Ni wire electrodes

Firstly we explored the deposition of Ag on Ni wire electrodes via a galvanic replacement reaction between Ag^+ and Ni wire under various conditions, i.e., by changing the concentration of AgNO_3 (typically, 0.10 mM and 1.0 mM) and the immersion time of Ni wire in the AgNO_3 solutions (typically, 10 min and 1 h). The deposition of Ag was evaluated by observing CVs in 1.0 M NaOH aqueous solutions using the Ag/Ni wire electrodes prepared as described above. In the case of Au deposition on Ni wire [5], the amount of Au deposited on the Ni wire was considerably influenced by the concentration of HAuCl_4 and the immersion time. Thus, we had expected some changes in the amount of Ag deposited on the Ni wire electrodes on changing the conditions. However, the CV results showed that the amount of Ag deposited did not change much on varying the concentration of the precursor or the immersion time.

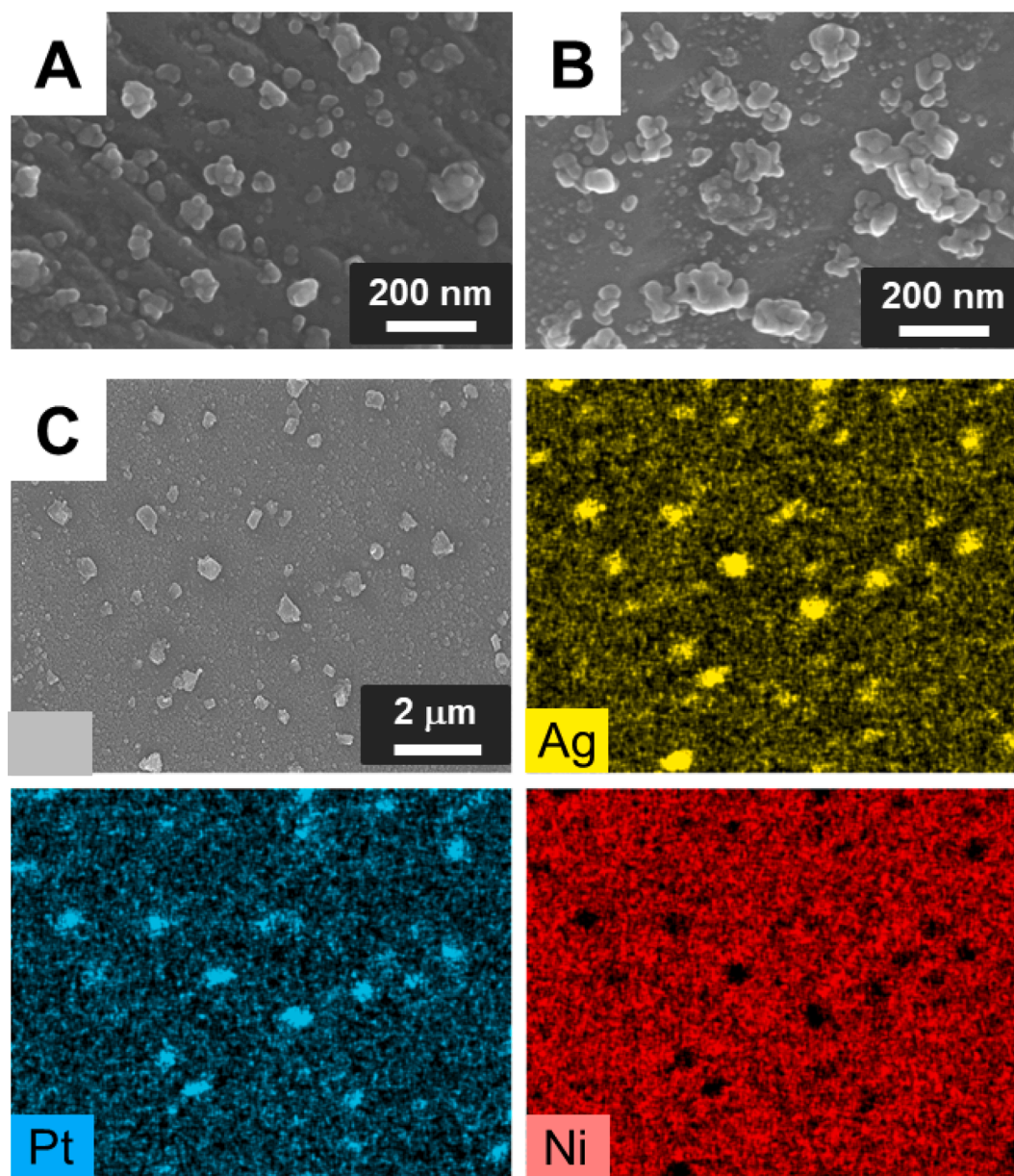


Fig. 3. (A, B) Typical FE-SEM images of the surfaces of (A) a Ag/Ni wire electrode and (B) a Pt-modified Ag/Ni wire electrode. (C) Results of EDS analysis for a Pt-modified Ag/Ni wire electrode showing a SEM image and element mapping of Ag, Pt and Ni. The Ag/Ni wire electrode in (A) was prepared by treating Ni wire in an aqueous solution of 1.0 mM AgNO_3 for 10 min, and the Pt-modified Ag/Ni wire electrode (B, C) was prepared by treating a Ag/Ni wire electrode in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min.

Fig. 1 shows CVs recorded using (A) a Ag/Ni wire electrode prepared with 1.0 mM AgNO_3 and an immersion time of 10 min and (B) a Ag disk electrode. The redox response shown in Fig. 1A did not change much even when the concentration of AgNO_3 was reduced to 0.10 mM, or the immersion time increased to 1 h. Thus, it is inferred that the deposition of Ag did not continue to increase, but rather terminated after a certain amount of Ag had been deposited. Comparing the current densities divided by geometrical area in Fig. 1A and B, the area of Ag on the Ag/Ni wire electrodes is apparently smaller than that of the Ag disk electrode. Hence, it is considered that Ag deposition terminated long before the whole Ni surface was covered. When the galvanic replacement deposition of Ag on electrodeposited Ni layers was reported previously [20], the amount of deposited Ag was also small.

3.2. Pt-modification on Ag/Ni wire electrodes

Next, modification with Pt was examined by treating Ag/Ni wire electrodes in aqueous solutions of K_2PtCl_4 . More precisely, a Ag/Ni wire electrode prepared by immersing a piece of Ni wire in an aqueous solution of 1.0 mM AgNO_3 for 10 min was treated in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min. Fig. 2A shows a CV of 1.0 M ethanol in 1.0 M NaOH aqueous solution recorded with the Pt-modified Ag/Ni wire electrode. To obtain a stable CV response, we repeated cyclic potential scans, and the CV at the 10th scan is shown in Fig. 2A. Fig. 2B and C show the CVs at the 10th scan recorded using a Pt-deposited Ni wire electrode prepared by immersing a piece of Ni wire in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min, and a Pt disk electrode, respectively.

Comparing the peak current values in the positive-going scans at ca. -0.3 V between Fig. 2A (24 mA cm^{-2}) and Fig. 2B, C (0.99 and 0.97 mA

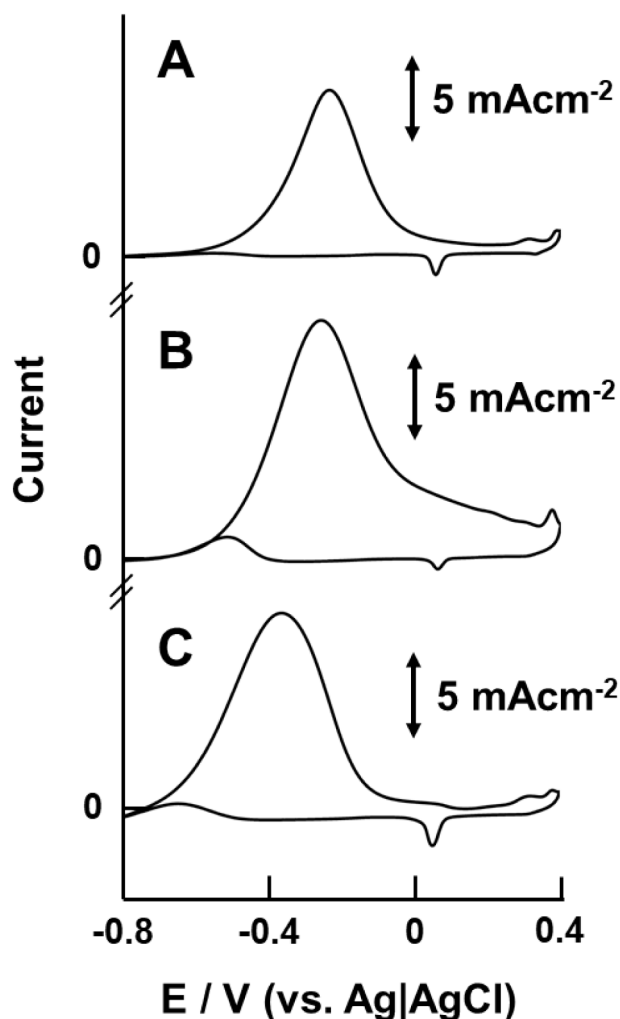


Fig. 4. Cyclic voltammograms of (A) methanol, (B) 1-propanol and (C) 2-propanol in 1.0 M NaOH aqueous solution recorded with a Pt-modified Ag/Ni wire electrode. The concentration of the alcohols was 1.0 M. Scan rate: 50 mV/s. The CVs of the 10th scan are shown.

cm^{-2}), it is apparent that modification of the Ag/Ni wire electrode with Pt enhanced its electrocatalytic capability for ethanol oxidation. In addition to the electrocatalytic responses for ethanol, the small redox responses in Fig. 2A (at 0.37 V and 0.07 V) are those of deposited Ag on Ni wire, and those in Fig. 2B (0.37 V and 0.31 V) are those of the Ni base. Because these are surface redox processes, a remarkable increase in the electrocatalytic response to ethanol in Fig. 2A is evident.

The CV in Fig. 2B indicates that the amount of Pt deposited was much smaller when Ni wire was treated in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min. Because the same treatment of a Ag/Ni wire electrode brought about an increase in electrocatalytic current as shown in Fig. 2A, it is clear that pre-deposition of Ag has a significant effect in promoting Pt modification.

The electrocatalytic response of ethanol (Fig. 2A) is similar to those observed using various Ag-Pt binary electrocatalysts [10–12] and Pt electrocatalysts [21], while the peaks in the reverse, negative-going scans were found to be comparable to the peaks in the positive-going scans using other Ag-Pt binary electrocatalysts [13,14]. So, some synergistic effects with Ag may be expected, in addition to enhancing modification with Pt. However, the CV responses change during cyclic potential scans, including those recorded with the Pt disk electrode. Thus, a careful evaluation of the electrocatalytic responses for ethanol should be carried out in further work.

3.3. Surface images of Pt-modified Ag/Ni wire electrodes

Fig. 3A and B shows typical FE-SEM images of the surfaces of (A) a Ag/Ni wire electrode and (B) a Pt-modified Ag/Ni wire electrode. When Fig. 3A and B were observed at higher magnifications, taking several measurements at each magnification, it was confirmed that Ag deposits mostly less than 100 nm in size were formed after treating Ni wire in an aqueous solution of AgNO_3 . After treating a Ag/Ni wire electrode in an aqueous solution of 1.0 mM K_2PtCl_4 for 10 min, the shapes of the Ag deposits were somewhat changed, as shown in Fig. 3B. However, in general, the effects were small enough not to change the shape and size of Ag deposits drastically. Fig. 3C shows the results of EDS analysis of the surface of a Pt-modified Ag/Ni wire electrode. The overlap in the location of Ag and Pt is confirmed by this result. Thus, it is considered that treatment with K_2PtCl_4 produces Pt mainly on the Ag deposits.

The galvanic replacement reactions between PtCl_4^{2-} (or PtCl_6^{2-}) and Ag have been well documented [15–17]. Because the presence of Cl^- makes the redox potential of Ag^+/Ag negative by forming AgCl, spontaneous galvanic replacement reactions should occur to form Pt(0) with the release of AgCl when Ag is used as the base material [15–17]. However, in the present case (the preparation of Pt-modified Ag/Ni electrodes), Ni^{2+} can be released from areas of bare Ni to promote modification with Pt, utilizing the larger potential gap between $\text{PtCl}_4^{2-}/\text{Pt}$ and Ni^{2+}/Ni (compared with AgCl/Ag) with the electrical contact of Ag deposits between Ni and Pt. More detailed studies are necessary to clarify the exact states of Pt(0) present on Ag and the corresponding formation mechanisms.

3.4. Electrocatalytic oxidation of alcohols on Pt-modified Ag/Ni wire electrodes

Fig. 4 shows CVs of alcohols in 1.0 M NaOH aqueous solution recorded with Pt-modified Ag/Ni wire electrodes. In addition to the electrodes' electrocatalytic capability for ethanol (Fig. 2A), electrocatalytic oxidation was also confirmed for methanol, 1-propanol and 2-propanol, as shown in Fig. 4. The CV responses for the four alcohols all resemble each other, with small redox peaks representing Ag deposited on Ni and smaller oxidation peaks in the reverse, negative-going scans.

Because different electrocatalytic responses have been reported when comparing only methanol and ethanol [21], a comprehensive discussion of the changes in current magnitude and peak potentials between the four alcohols would not be easy. However, there is one interesting result that is different from an earlier report [22]: Fig. 4 shows that the current value of the positive-going peak of 2-propanol (11 mA cm^{-2}) is larger than that of methanol (9.1 mA cm^{-2}). The electrocatalytic current of 2-propanol was reported to be much smaller when using a Pt/CNT modified GC electrode [22] and a Pt disk electrode [23]. In addition, a noticeable decrease in the electrocatalytic current over repeated scans for 2-propanol was reported when using a Pt disk electrode. This was believed to be due to poisoning by acetone [24]. Our results also show that the current density values at the 10th scans were 0.17 and 0.10 mA cm^{-2} using a Pt-deposited Ni wire electrode and a Pt disk electrode, respectively (data not shown), which might be due to poisoning.

However, the electrocatalytic responses were not poisoned in the case of the Pt-modified Ag/Ni electrodes, and the electrocatalytic response for 2-propanol (Fig. 4C) was observed to be similar to that of the other three alcohols. Thus, the Pt-modified Ag/Ni wire electrodes may have some specific characteristics favouring the oxidation of 2-propanol.

4. Conclusions

We compared the electrocatalytic responses of four alcohols, i.e., methanol, ethanol, 1-propanol and 2-propanol, using Pt-deposited Ni wire electrodes and Pt-modified Ag/Ni wire electrodes. The Pt-modified

Ag/Ni wire electrodes showed a remarkable increase in the electrocatalytic oxidation currents in the positive-going scans, while the corresponding effect with the Pt-deposited Ni wire electrodes was much smaller. This difference implied that the presence of Ag deposits on the Ni wire promoted modification with Pt, which was confirmed by the FE-SEM images and EDS results.

While the amount of Pt deposited directly on the Ni wire was quite small, previous reports showed that syntheses of vertically aligned hollow Pt nanotubes [25] and Pt nanoparticles [26] were possible, scarifying Ni nanorods and Ni nanoparticles, respectively. The reason for deposition of less Pt on the Ni wire is therefore unclear. However, it should be noted that Ni²⁺ could be released from the Ni wire to form Pt (0)-on-Ag deposits, unlike the direct galvanic replacement reactions to form Pt(0) by scarifying Ag [15–17]. Furthermore, it is also unclear why the amount of Ag deposited on the Ni wire was limited.

However, as a method to promote Pt modification of Ni wire, the pre-treatment with an aqueous solution of AgNO₃ was quite effective. Previously deposited Ag has been shown to be useful in modifying a Ni surface with Pt, although details of the Pt deposition should be explored further, together with a more in-depth study of the electrocatalytic properties. Even though the proposed preparation involves two steps, the simplicity of the treatment, typically taking 10 min in aqueous solutions, is an advantage. We have previously proposed the use of Ni microparticles as a supporting material for electrocatalytic applications [7], and the approach presented here is a promising method for modifying Ni microparticles with Pt.

CRedit authorship contribution statement

Fumikazu Sato: Investigation. **Sota Funo:** Investigation. **Zhiwei Cai:** Investigation. **Gang Chang:** Supervision. **Yunbin He:** Supervision. **Munetaka Oyama:** Writing - original draft, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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