Electrochromic properties of Ni oxide thin films in diluted acidic electrolytes and their stability

Yoshio Abe[a], Se-Hee Lee[b], Esra Ozkan Zayim[c], C. Edwin Tracy[b], J. Roland Pitts[b], and Satyen K. Deb[b]

[a]Kitami Institute of Technology, Kitami 090-8507, Japan

[b]National Renewable Energy Laboratory, Golden, Colorado 80401, USA

[c]Istanbul Technical University, Maslak, Istanbul 80626, Turkey

Abstract

Electrochromic (EC) properties of sputtered Ni oxide films have been examined in 1M KCl + H_2SO_4 acidic aqueous solutions with H_2SO_4 concentrations of 0–50 mM. EC coloration efficiency comparable to that in alkaline electrolytes was obtained in all the solutions and no remarkable degradation in charge capacity was observed up to 100 cycles. These results offer support for the practical construction of efficient complementary EC devices using dilute acidic aqueous electrolytes.

Keywords

Ni oxide thin film, electrochromic, acidic aqueous electrolyte, cycling stability

1. Introduction

Electrochromic (EC) materials [1,2] can change their optical properties (darken and lighten) by application of a small reversible dc voltage, and EC devices are being developed in applications for "smart" energy efficient windows, anti-glare automobile rearview mirror, sunroofs, and visors [3-6]. A typical EC device consists of a stack of thin films having an EC layer, an ion-conducting layer and an ion-storage layer sandwiched between two transparent conducting oxide layers. A complementary EC device employs a cathodically coloring film (such as W oxide) as an EC layer and an anodically coloring film (such as Ni oxide) as an ion storage layer to improve EC coloration efficiency and to obtain larger color changes with smaller current densities [3,6-9]. One of the problems associated with combining W oxide and Ni oxide films is their chemical incompatibility. W oxide is relatively stable in an acidic environment whereas it dissolves in a basic one. On the other hand, Ni oxide is relatively stable in a basic environment but is unstable in an acidic one [10,11]. Therefore, EC properties of Ni oxide films in aqueous electrolytes have been generally studied in basic solutions (such as KOH and NaOH) [12-20], and reports on the EC properties in acidic electrolytes are few. However, Lee *et al.* [21] reported on the EC properties of NiO/Ta_2O_5 nano-composites using pH neutral KCl aqueous solutions and our previous papers [22,23] indicated high EC coloration efficiencies of about 30 cm^2/C for sputtered Ni oxide films in dilute acidic solutions. From this perspective, we examined the possibility of employing acidic electrolytes for use with Ni oxide anodic EC materials. In this study, the EC properties and the stability of Ni oxide films have been examined in aqueous solutions with various acidic concentrations.

2. Experimental

Ni oxide thin films with thicknesses of 400 nm were concurrently deposited on glass substrates coated with a transparent-conducting layer of F doped SnO_2 for electrochemical and EC characterizations and on plain glass substrates for structural analyses. These films were deposited from a Ni target (4 inches in diameter) which was sputtered reactively in an Ar/O_2 atmosphere using a radio-frequency (RF) magnetron sputtering system as reported in previous papers [22,23]. Although optical density changes of the Ni oxide films increase with oxygen flow concentration, $[O_2/(Ar+O_2)] \times 100\%$ [23], the films deposited at an oxygen flow ratio of 100% tended to peel off during cycling test. Therefore, oxygen flow ratios of 30–50% were used in this study. The total gas flow rate, RF power and substrate-target distance were standardized to 30 standard cubic centimeter per minute (sccm), 60 W and 5 cm, respectively. Total sputtering gas pressure was consistently maintained at 1.5 Pa with no intentional substrate heating. The maximum substrate temperature during sputtering was estimated to be 60°C at most.

Crystal structure was characterized by X-ray diffraction (XRD) using Cu Kα radiation. Cyclic voltammetry (CV) and *in-situ* optical measurements were carried out using Ag/AgCl and Pt as reference and counter electrodes. Mixed aqueous solutions of 1M KCl + H_2SO_4 with H_2SO_4 concentrations of 0–50 mM were used as electrolytes. CV measurements were carried out with a voltage scan rate of 10 mV/sec. Charge capacity was calculated by integrating the charging and discharging current density of the CV curves. The optical densities of the Ni oxide films were measured during the constant current

discharge (current density of 20 $\mu A/cm^2$) from 1.0 V to 0 V vs. Ag/AgCl. EC coloration efficiency (η) was calculated by the following equation:

$$\eta = \Delta OD/ \Delta Q,$$

where ΔOD is the change in optical density ($\Delta OD = \log_{10} (T_b/T_c)$, where T_b and T_c are bleached and colored transmittance) and ΔQ is the charge density. *In situ* optical modulation was measured using a laser diode at 670 nm wavelength and transmittance spectra after bleaching and coloring were measured by a spectrophotometer.

3. Results and discussion

The structures of the Ni oxide thin films deposited on glass substrates have been studied by XRD and crystalline diffraction peaks due to cubic (rock salt) NiO are observed [22,23]. However, the peak intensities are very weak and the peaks are broad, indicating a nano-crystalline structure with grain sizes of a few nanometers.

The transmittance spectra of an FTO-coated glass substrate and a Ni oxide film deposited on a similar substrate are shown in Fig. 1. The film was colored and bleached by applying constant voltages of 1V and 0V (vs Ag/AgCl reference electrode), respectively, for 5 min in a 1 M KCl + 0.5 mM H_2SO_4 solution. The colored and bleached transmittance spectra in KCl +H_2SO_4 are basically similar in character to those in alkaline electrolytes [12,13,16,23]. As reported in a previous paper [19] valance changes of Ni ions, Ni^{2+} (bleached state) $\leftrightarrow Ni^{3+}$ (colored state), is thought to be the underlying mechanism for the optical modulations of the Ni oxide films.

Fig. 2 shows the change in optical density (ΔOD) during the constant current discharge (current density of 20 μA/cm^2) from 1.0 V to 0 V in the solutions with various H$_2$SO$_4$ concentrations. A maximum ΔOD of 0.49 was obtained for a H$_2$SO$_4$ concentration of 0.5 mM corresponding to the increase of charge capacity [22]. Fig. 3 shows the EC coloration efficiency as a function of H$_2$SO$_4$ concentration. Nearly constant EC coloration efficiencies on the order of 30 cm^2/C were determined for the Ni oxide films regardless of H$_2$SO$_4$ concentration. These values are comparable to those reported for sputtered Ni oxide thin films in KOH and NaOH alkaline electrolytes (31–36 cm^2/C at wavelengths of 550–633 nm) [13,15,17,18] because the coloration efficiency of Ni oxide was reported to increase with decreasing wavelength in the visible spectral region [24].

The chemical stability of the Ni oxide films in acidic solutions is an important problem because it is indicated that NiO is thermodynamically unstable in acidic aqueous solutions by the Pourbaix diagram [10], and Azens *et al.* [11] used a protective film to solve this problem. CV cycling tests of the Ni oxide thin films were carried out in 1 M KCl, 1 M KCl + 0.5 mM H$_2$SO$_4$ and 1 M KCl + 2 mM H$_2$SO$_4$ solutions, and CV curves after cycling for 5, 20 and 100 cycles are shown in Fig. 4. No remarkable changes in the CV curves are observed after cycling in 1M KCl, and a slight decrease of current density in the low voltage region and a slight increase of current density in the middle and high voltage regions are observed in 1 M KCl + 0.5 mM H$_2$SO$_4$ and 1 M KCl + 2 mM H$_2$SO$_4$ solutions. The charge capacity of the Ni oxide films after cycling is shown in Fig. 5. Upon initial cycling, the charge capacity increases slightly and stabilizes after 20 cycles in 1 M KCl + 0.5 mM H$_2$SO$_4$ and 1 M KCl + 2 mM H$_2$SO$_4$, and that in 1 M KCl is almost constant up to

100 cycles. These results suggest that the dissolution rates of the Ni oxide films in the acidic aqueous solutions are very low. The increase in the charge capacity during initial cycling period was also observed for NiO films in a KOH electrolyte, and it was correlated to a chemical conversion from NiO to $Ni(OH)_2$ at the surface of NiO grains [25]. Although the electrochemical reaction mechanisms in $KCl + H_2SO_4$ are not clear, it is speculated that some kind of chemical conversion at the surface of NiO grains occurred in the $KCl + H_2SO_4$ acidic aqueous solutions.

The high EC efficiencies, large ΔODs and good cycling stability of the Ni oxide films in dilute acidic solutions indicate that Ni oxide thin films can be used in the construction of complementary EC devices with cathodically coloring W oxide using an aqueous electrolyte. Though no remarkable changes were observed for the Ni oxide films after 100 cycles, we are planning a longer cycling test of the Ni oxide films in the future because it is necessary to secure longer cycling durability for practical applications.

4. Conclusions

Electrochemical and electrochromic properties of Ni oxide thin films have been measured in $KCl + H_2SO_4$ acidic aqueous solutions. The Ni oxide films exhibit coloration efficiencies of approximately 30 cm^2/C and a maximum ΔOD of 0.49. CV cycling tests up to 100 cycles indicate no remarkable degradation in the acidic solutions. These results indicate the possibility of the construction of complementary EC devices using dilute acidic aqueous solution as an electrolyte.

References

[1] S. K. Deb, Philos. Mag. 27 (1973) 801-822.

[2] C. G. Granqvist, Handbook of Inorganic Electrochromic Materials (Elsevier, Amsterdam, 1995).

[3] J. Nagai, G. D. McMeeking, Y. Saitoh, Sol. Energy Mater. Sol. Cells 56 (1999) 309-319.

[4] S. K. Deb, S.-H. Lee, C. E. Tracy, J. R. Pitts, B. A. Gregg, H. M. Branz, Electrochimica Acta 46 (2001) 2125-2130.

[5] C. M. Lampert, Sol. Energy Mater. Sol. Cells 76 (2003) 489-499.

[6] A. Azens, G. Gustavsson, K. Karmhag, C. G. Granqvist, Solid State Ionics 165 (2003) 1-5.

[7] N. A. O'Brien, J. Gordon, H. Mathew, B. P. Hichwa, Thin Solid Films 345 (1999) 312-318.

[8] Y.-C. Nah, K.-S. Ahn, Y.-E. Sung, Solid State Ionics 165 (2004) 229-233.

[9] C. G. Granqvist, E. Avendaño, A. Azens, Thin Solid Films 442 (2003) 201-211.

[10] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions (National Association of Corrosion Engineers, Houston, 1974) 2nd ed. 330-342.

[11] A. Azens, G. Vaivars, M. Veszelei, L. Kullman, C. G. Granqvist, J. Appl. Phys. 89 (2001) 7885-7887.

[12] J. S. E. M. Svensson and C. G. Granqvist, Appl. Phys. Lett. 49 (1986) 1566-1568.

[13] D. A. Wruck, M. A. Dixon, M. Rubin, S. N. Bogy, J. Vac. Sci. Technol. A, 9 (1991) 2170-2173.

[14] A. Agrawal, H. R. Habibi, R. K. Agrawal, J. P. Cronin, D. M. Roberts, R. Caron-Popowich, C. M. Lampert, Thin Solid Films 221 (1992) 239-253.

[15] M. Kitao, K. Izawa, K. Urabe, T. Komatsu, S. Kuwano, S. Yamada, Jpn. J. Appl. Phys. 33 (1994) 6656-6662.

[16] K. Yoshimura, T. Miki, S. Tanemura, Jpn. J. Appl. Phys. 34 (1995) 2440-2446

[17] F. F. Ferreira, M. H. Tabacniks, M. C. A. Fantini, I. C. Faria, A. Gorenstein, Solid State Ionics 86-88 (1996) 971-976.

[18] K.-S. Ahn, Y.-C. Nah, Y.-E. Sung, Jpn. J. Appl. Phys. 41 (2002) L533-L535.

[19] I. Bouessay, A. Rougier, B. Beaudoin, J. B. Leriche, Appl. Surf. Sci. 186 (2002) 490-495.

[20] J.-Y. Park, K.-S. Ahn, Y.-C. Nah, H.-S. Shim, Y.-E. Sung, J. Sol-Gel Sci. Technol. 31 (2004) 323-328.

[21] S.-H. Lee, C. E. Tracy, Y. Yan, J. R. Pitts, S. K. Deb, Electrochem. Solid-State Lett., 8 (2005) A188-A190.

[22] Y. Abe, S.-H. Lee, C. E. Tracy, J. R. Pitts, S. K. Deb, Electrochem. Solid-State Lett. 9 (2006) J31-J33.

[23] Y. Abe, S.-H. Lee, E. Ozkan-Zayim, C. E. Tracy, J. R. Pitts, S. K. Deb, Jpn. J. Appl. Phys. 45 (2006) 7780-7783.

[24] C. R. Ottermann, A. Temmink, K. Bange, Thin Solid Films 193/194 (1990) 409-417.

[25] I. Bouessay, A. Rougier, P. Poizot, J. Moscovici, A. Michalowicz, J-M. Tarascon, Electrochimica Acta 50 (2005) 3737-3745.

Figure captions

Fig. 1. Transmittance spectra of a FTO-coated glass substrate and a Ni oxide film deposited on a similar substrate. The coloration and bleaching of the Ni oxide film were measured in 1 M KCl + 0.5 mM H_2SO_4.

Fig. 2. Optical density change of Ni oxide films during negative voltage scan from 1.0 V to 0 V as a function of varying H_2SO_4 concentrations (0 to 50 mM). Optical density was measured *in situ* at a wavelength of 670 nm using current density of 20 $\mu A/cm^2$.

Fig. 3. EC coloration efficiency of Ni oxide films during negative voltage scan from 1.0 V to 0 V as a function of H_2SO_4 concentration. Optical density was measured *in situ* at a wavelength of 670 nm using current density of 20 $\mu A/cm^2$.

Fig. 4. Cyclic voltammogram images measured in (a) 1 M KCl, (b) 1 M KCl + 0.5 mM H_2SO_4 and (c) 1 M KCl + 2 mM H_2SO_4 solutions after cycling. The voltage scan rate was 10 mV/s.

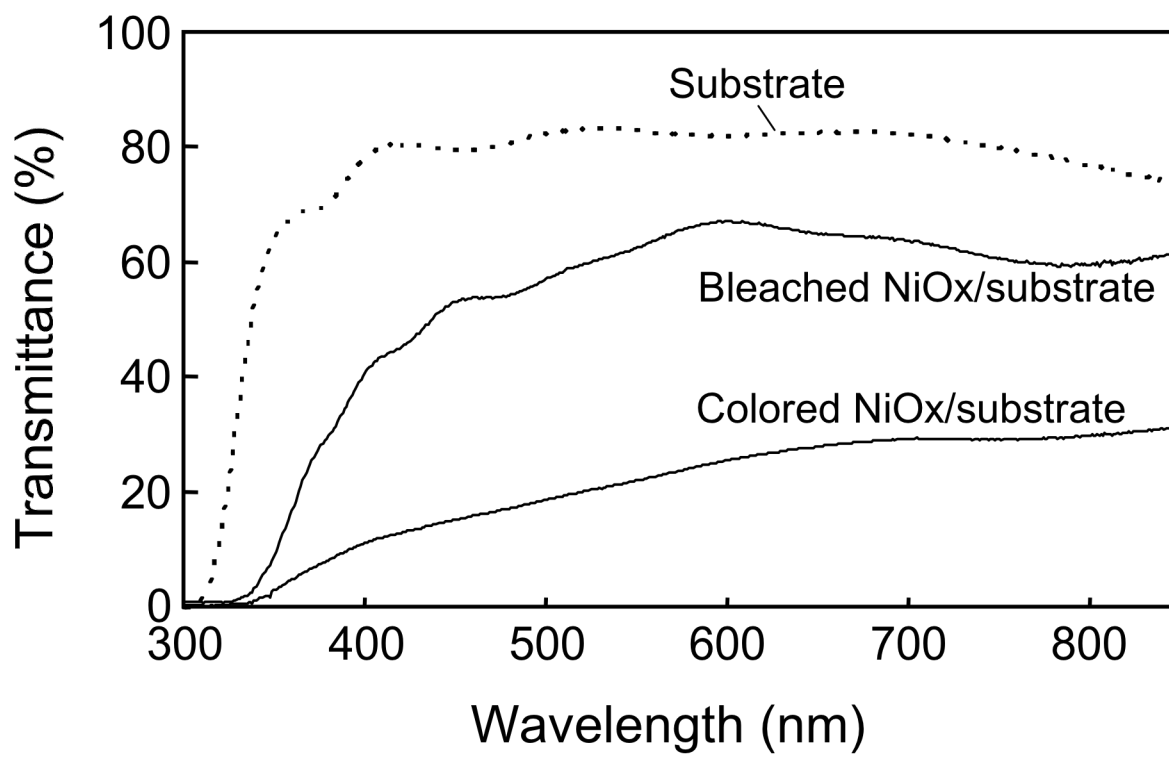Fig. 5. Cycling stability of charge capacity measured in 1 M KCl, 1 M KCl + 0.5 mM H_2SO_4 and 1 M KCl + 2 mM H_2SO_4 solutions. The voltage scan rate was 10 mV/s.
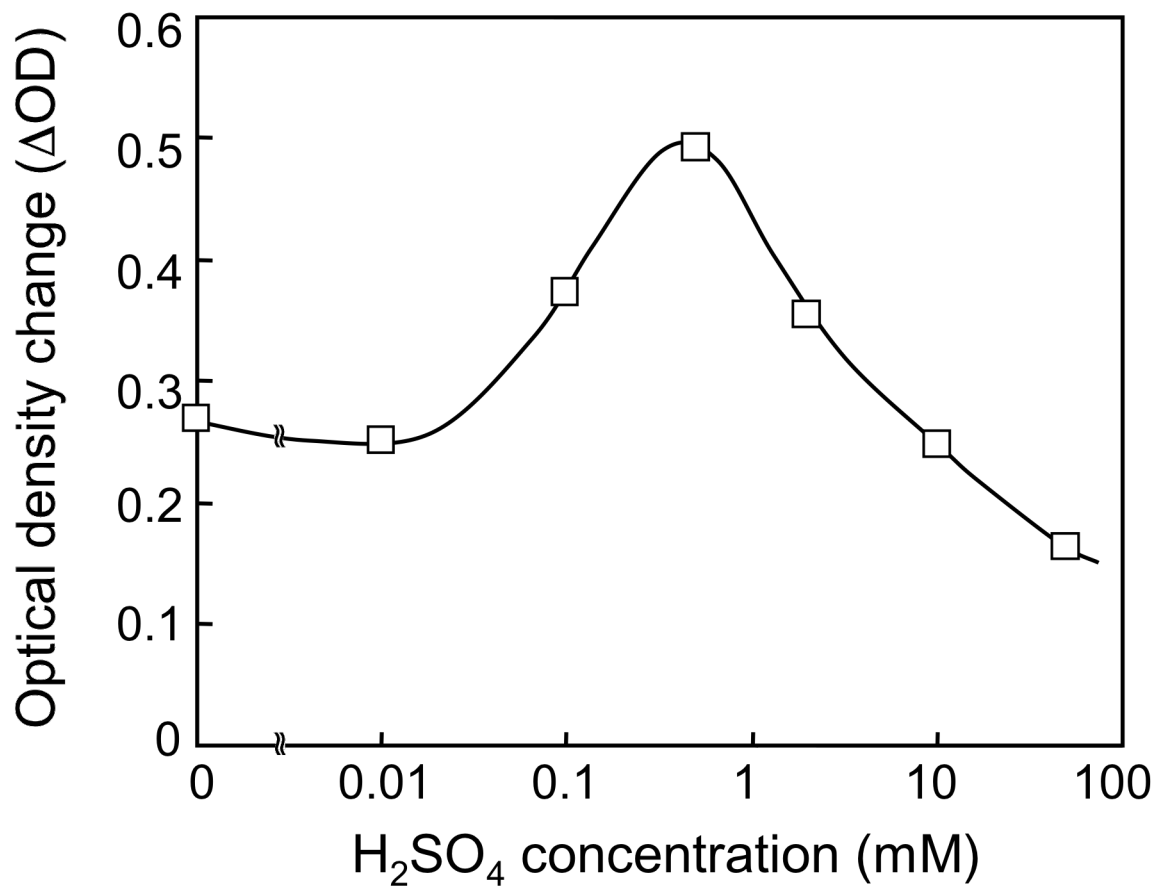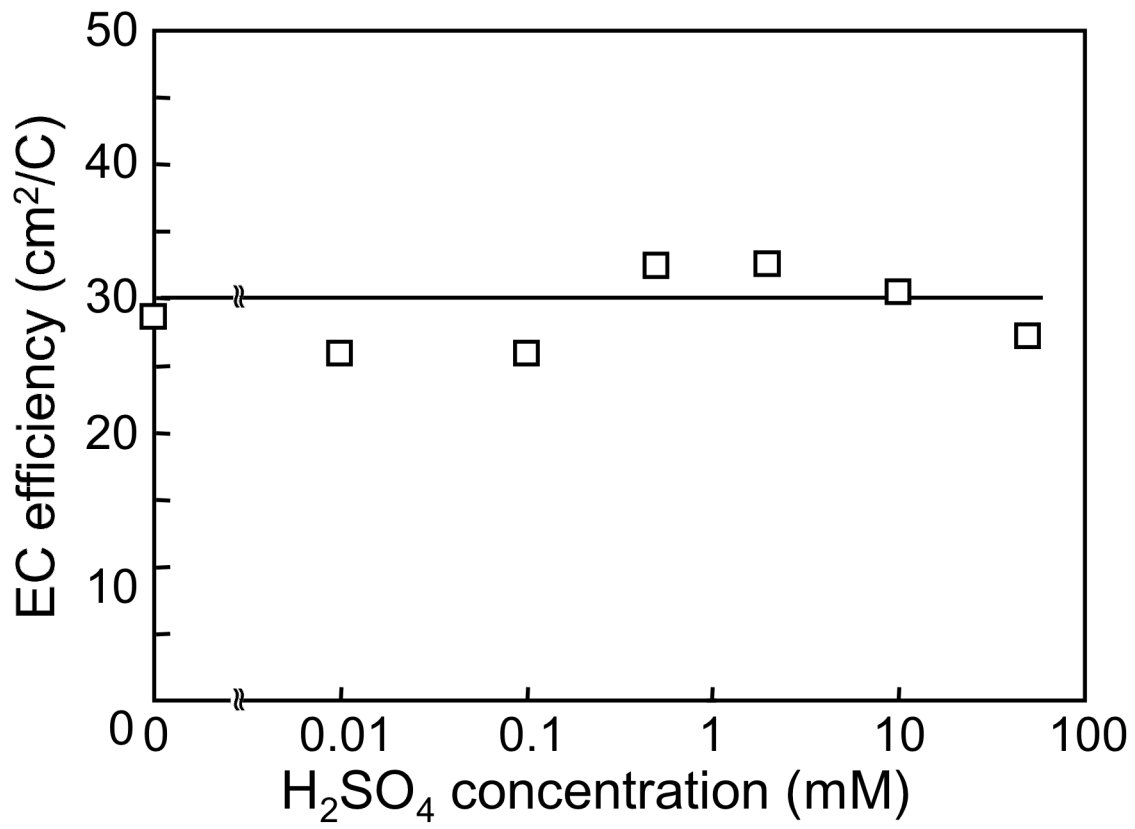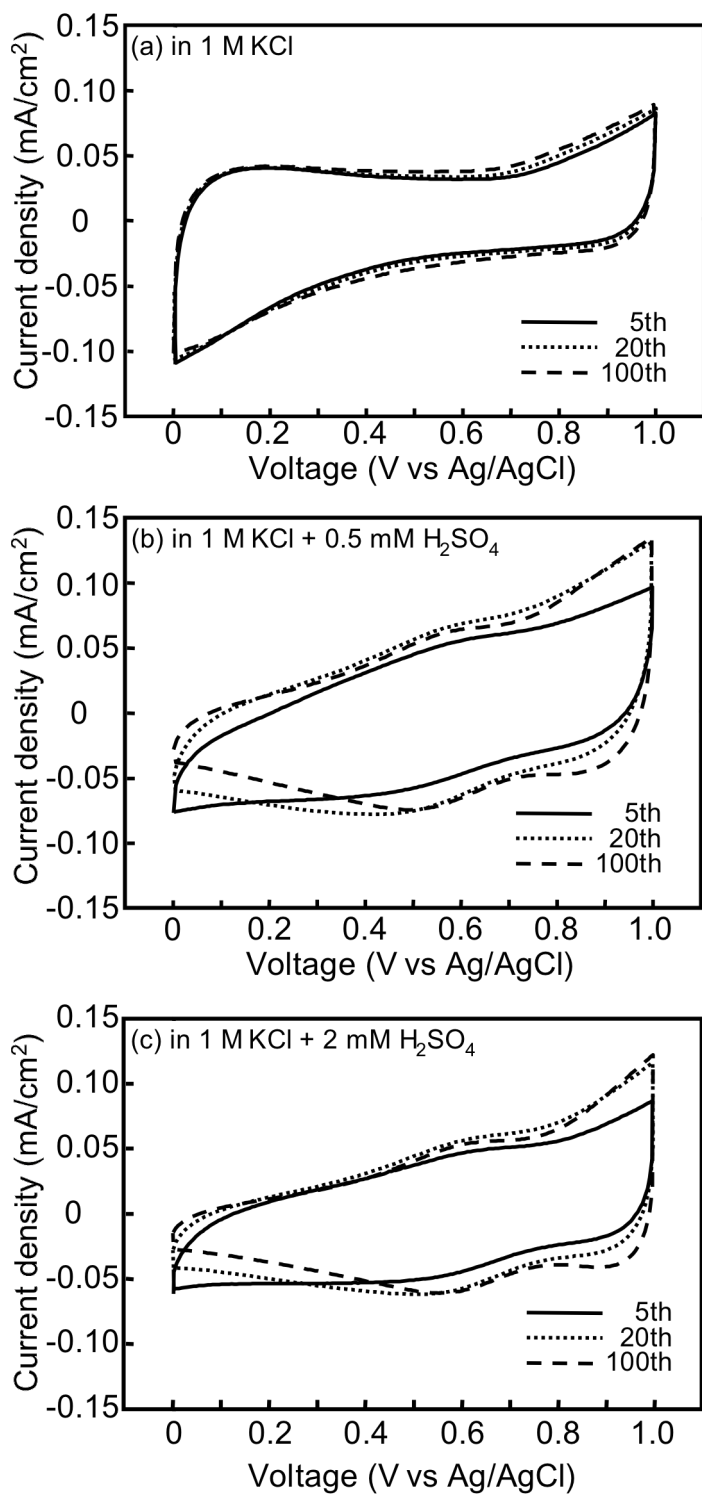
Fig. 1

Fig. 2

Fig. 3

Fig. 4

13

Fig. 5