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Selective micro-etching of duplex stainless steel for preparing manganese oxide supercapacitor electrode

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ABSTRACT

In this investigation, manganese oxide electrodes that incorporate selectively micro-etched duplex stainless steel (DSS) for supercapacitor applications were fabricated. The experimental results demonstrate that selective dissolution of the γ phase could result in the formation of α phase network, and vice versa. Controlling the extent of selective dissolution produces a surface with a concave–convex morphology, increasing the surface area. Manganese oxide could then be anodically deposited onto the etched dual phase steel current collector. The experimental results of cyclic voltammetry (CV) show that the specific capacitance increased with the etching depth of either the γ or the α phase. Additionally, selective dissolution occurred in α phase had a better effect on increasing the specific capacitance. The successful application of selective dissolution in fabricating a current collector was thus demonstrated.

1. Introduction

The charge storage capacity of a supercapacitor can be improved by increasing the electrode surface area. For a manganese oxide supercapacitor, the oxide film can be deposited on many substrates, which act as current collectors. Along with graphite [1–3], nickel [4,5] and other conductive materials [6,7], stainless steel can be used because it is inert in various supercapacitor electrolytes. Among the various grades of stainless steel, duplex stainless steels (DSSs) with a relatively high Cr content are particularly attractive because of their higher corrosion resistance in such electrolytes as KOH, Na_2SO_4 solutions and others.

DSS comprises austenitic (γ) and ferritic (α) phases. The former has a face-centered cubic (FCC) crystal structure while the latter is body-centered cubic (BCC). Each phase has a specific chemical composition, and therefore manifests a distinct electrochemical nature in certain electrolytes. Previous studies have demonstrated that the mixed H_2SO_4/HCl solutions yield two anodic peaks in the active-to-passive transition region of the potentiodynamic polarization curves of 2205 DSS. Selective (preferential) dissolution can occur at each of these characteristic potentials [8]. Accordingly, Tsai and Chen developed a novel procedure that involves selective micro-etching reaction for fabricating micro-networks or rods with an exclusively γ or α phase from dual-phase stainless steel [9]. After one of the constituent phases is selectively dissolved in a specific mixed H_2SO_4/HCl solution, the concave/convex microstructure of a dual-phase stainless steel can give rise to an increase in surface area. This etched stainless steel may be advantageous for use as an electrode substrate for supercapacitor applications.

Manganese oxide has been found to be a promising substitute for ruthenium oxide as the electrode material for supercapacitors [10,11]. It can be anodically deposited under either constant potential [12] or constant current [13] conditions, to prepare a supercapacitor electrode using graphite or nickel substrate. The use of a substrate with a high specific surface area is considered to increase the specific capacitance of a manganese oxide electrode (in terms of $F\,g^{-1}$). Coating manganese oxide onto a stainless steel substrate with a concave/convex feature, as presented in Fig. 1, may yield a high specific capacitance. Therefore, this investigation examines the feasibility of increasing the specific capacitance of a manganese oxide electrode by the selective micro-etching of a DSS substrate.

2. Experimental

2.1. Specimen preparation

Table 1 presents the chemical composition of the 2205 DSS rod used in this study. After solid solution heat treatment at 1100 °C for 30 min, the α/γ volume ratio was approximately 1.13, where α was the continuous phase. Table 1 also presents the respective

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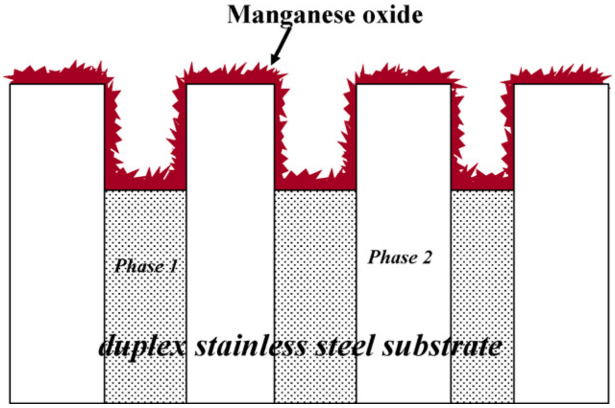

Fig. 1. Schematic diagram showing the cross-sectional feature of a selectively etched 2205 DSS coated with manganese oxide.

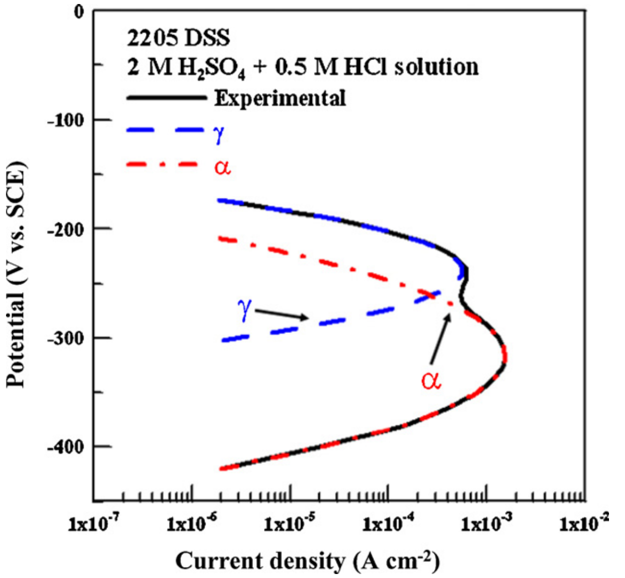

Fig. 2. Full and dissociated potentiodynamic polarization curves of the active-to-passive transition region of 2205 DSS in mixed 2 M H_2SO_4 + 0.5 M HCl solution.

chemical compositions of α and γ phases, analyzed by energy dispersive spectrometry (EDS). The solution heat-treated steel rod was then cut into a 2 mm-thick disc with a cross-sectional area of 1 cm × 1 cm. This disc was connected to a copper wire, and mounted in epoxy resin, before being ground using SiC paper to a grit finish of #1000. Finally, the mounted specimen was cleaned ultrasonically in distilled water before selective etching and manganese oxide coating.

2.2. Selective etching

A mixed 2 M H_2SO_4 + 0.5 M HCl solution was adopted herein. The etching potentials were determined from the potentiodynamic polarization curve of 2205 DSS. The procedure for measuring the electrochemical polarization curve has been elucidated elsewhere [9]. Fig. 2 plots the potentiodynamic polarization curve in the active-to-passive transition region of 2205 DSS in mixed 2 M H_2SO_4 + 0.5 M HCl solution. The polarization curve can be dissociated into two distinct curves one for the γ phase and the other for α phase as presented in Fig. 2. The respective characteristic peak potentials, −260 and −320 mV (with respect to a saturated calomel electrode, SCE), were selected for potentiostatic etching of the γ and α phases, respectively. The etching time varied from 1 to 4 h. The specimens designated as A1, A2, and A4 were those of 2205 DSS etched at the characteristic potential for selective dissolution of the γ phase for 1, 2 and 4 h, respectively. Specimen A0 was not etched. Similarly, the specimens F0, F1, F2 and F4 were those with α phase selectively dissolved.

2.3. Anodic deposition of manganese oxide

Manganese oxide was electroplated onto each of the various etched 2205 DSS substrates by anodic deposition in a neutral 0.25 M $MnSO_4$ plating solution at room temperature. Anodic deposition was performed in a three-electrode system at a constant applied potential, as reported upon elsewhere [14,15]. During the deposition, the substrate was held as the anode while a platinum sheet and an SCE were used as the counter electrode and the reference electrode, respectively. An EG&G Princeton Applied Research model 263 potentiostat was adopted to apply a total charge of 0.2 C at a constant potential of 0.9 V. After electrodeposition, the electrode was dried in air.

2.4. Cyclic voltammetry

The supercapacitive behavior of the manganese oxide electrode was characterized by cyclic voltammetry (CV) in 0.1 M Na_2SO_4 solution at room temperature. The test cell was a three-electrode system of which the manganese oxide electrode was the working electrode. A platinum sheet and an SCE were used as the counter electrode and the reference electrode, respectively. The measuring instrument was an Autolab PGSTAT302 potentiostat. The potential was scanned in a potential range of 0–1 V. The CV scan rate was varied from 5 to 100 mV s^{-1}.

2.5. Surface morphology and chemical state analyses

The surface morphologies and cross-section images of etched 2205 DSS and those coated with manganese oxide were examined with a scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) was adopted to analyze the chemical state of the manganese oxides. The measurements were made using an ESCA 210 (VG Science Ltd.) spectrometer. Monochromatic Al Kα (1486.6 eV) radiation was the X-ray source. The pressure in the analyzing chamber was about 1×10^{-9} Torr during the measurement.

Table 1
Chemical compositions (in wt.%) of 2205 DSS and the constituent ferritic (α) and austenitic (γ) phases.

Element	Fe	Cr	Ni	Mo	Mn	Si	C	Cu	P	S	N
2205 DSS	Bal.	22.4	5.42	3.24	1.43	0.41	0.014	0.21	0.025	0.004	0.198
α-Phase[a]	Bal.	23.5	4.8	3.5	1.0	–	–	–	–	–	–
γ-Phase[a]	Bal.	20.5	7.2	1.0	2.0	–	–	–	–	–	–

[a] Energy dispersive spectrometer (EDS).