



AC charging/discharging of de-alloyed Si–Al–V alloy ribbons

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ABSTRACT

In anticipation of prompt ac charging/discharging characteristics, the capacitance of de-alloyed $\text{Si}_{1-x}(\text{Al}_{0.5}\text{V}_{0.5})_x$ ($x = 0.15, 0.2, 0.3$, and 0.4) alloy ribbons with resistivities of $0.01\text{--}4300\ \Omega\text{cm}$ was measured as a function of frequency between 1 MHz and 1 MHz , using exponential transient analysis for electric charging/discharging. The capacitance of de-alloyed $\text{Si}\text{--}7.5\text{ at.\%Al}\text{--}7.5\text{ at.\%V}$ obtained by prompt ($100\text{ ms--}25\text{ ns}$) charging/discharging decreased logarithmically from $105\ \mu\text{F}$ to 18 pF as frequency increased from 1 MHz to 10 kHz , and then saturated between 10 kHz and 1 MHz . From the observed electrode distance dependence on capacitance, we deduced that the alloy consisted of a distributed constant equivalent circuit (series with 1.2% parallel), analogous to electric double layer capacitors.

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1. Introduction

Generally, electric charge cannot be stored in metals (or alloys) without a dielectric open space. The ability to store charge in a centimeter-sized glassy alloy without dielectric open space, would lead to significant advancements in the field of not only electronic devices but also electric power applications. Recently, we found that the $(\text{Ni}_{0.36}\text{Nb}_{0.24}\text{Zr}_{0.40})_{90}\text{H}_{10}$ glassy alloy, showing Coulomb dot oscillation at room temperature [1] and a semi-true circular Nyquist diagram with total capacitance of $17.8\ \mu\text{F}$ [2], can be regarded as a dc/ac converting device having a large number of 0.23 nm -capacitors with femtofarad capacitance among its distorted icosahedral $\text{Zr}_5\text{Ni}_5\text{Nb}_3$ clusters (dots of ca. 0.55 nm in size [3]). In this material, hydrogen atoms flow into spaces outside the clusters, enlarging the spaces and resulting in the construction of zigzag tunnels of 0.23 nm average width because of the high pressure effect of hydrogen during electrolysis [4]. However, severe constraints on prompt discharging were observed experimentally for this material, because the electric charge behaves as a polarized glutinous liquid that is absorbed between pairs of metallic clusters [5]. This is known as electroadsorption [6]. In practice, we found that the low resistance of the $\text{Ni}\text{--}\text{Nb}\text{--}\text{Zr}\text{--}\text{H}$ glassy alloy in the input circuit prevented its prompt discharging to an output circuit with larger resistance. Rapid, powerful, and energy-rich storage effects in such materials are necessary for future electronic devices and electric power applications such as hybrid electric vehicles and backup power supplies.

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In anticipation of prompt charge/discharging, we reported electric storage characteristics for de-alloyed $\text{Si}\text{--}\text{Al}$ alloy ribbons with a capacitance of $102\ \mu\text{F}$ at 1 MHz [7]. We found that the de-alloyed specimen had an electronic transport structure similar to that of a metal–semiconductor junction (i.e. Schottky junction) [8], which is attributable to the residue of Al in the Si skeleton. For the fractal structure of the de-alloyed $\text{Si}\text{--}\text{Al}$ alloy capacitor, we assumed that the structure resembles that of an electric double-layer capacitor (EDLC), which is composed of a distributed constant equivalent circuit of active carbon (R) and electrolyte (C) [9,10]. The Si skeleton and Al backbone is to an electron what active carbon is to the electrolyte solution in EDLC. However, the transport rate of the electrons contributes to prompt charging/discharging, gaining an advantage over conventional batteries such as EDLC.

In this study, $\text{Si}\text{--}\text{Al}\text{--}\text{V}$ alloys were chosen as starting alloys for the formation of nanometer-sized porous structures with high resistivities of $10\ \mu\Omega\text{cm}$ to $4.3\text{ k}\Omega\text{cm}$ using a de-alloying method, with an aim to obtain further rapid charge/discharge characteristics rather than those of de-alloyed $\text{Si}\text{--}\text{Al}$ alloys.

2. Experimental

$\text{Si}\text{--}\text{Al}\text{--}\text{V}$ alloy ingots (compositions given in nominal atomic percentage) were prepared by arc-melting mixtures of Si (99.999% purity), Al (99.95% purity), and V (99.9% purity) in an argon atmosphere purified by Ti-gettering. Ribbon samples of $30\text{--}60\ \mu\text{m}$ in thickness and $1\text{--}2\text{ mm}$ in width were prepared from these ingots by rapid solidification of the melt on a single copper roller (Nisshin Gikken, Japan, NEV-A05-R10S) at a tangential velocity of 31.4 m/s . De-alloying of the samples was carried out for 259.2 ks in 1 N HCl solution to remove the Al content and then for 86.4 ks in condensed HNO_3 to eliminate the V content, at room temperature.

The sample structure was examined by X-ray diffraction (XRD, CN4012A1, Rigaku, Tokyo, Japan) in reflection mode with monochromatic $\text{Cu K}\alpha$ radiation. Surfaces of the de-alloyed specimens were examined by scanning electron microscopy (SEM, Hitachi S3800, Tokyo, Japan).

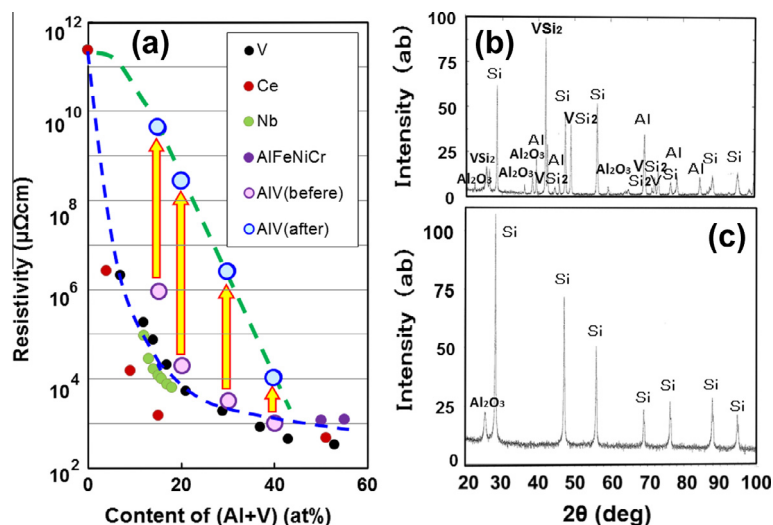


Fig. 1. (a) Electrical resistivities for Si–15, –20, –30 and –40 at.%(Al + V) alloys before and after HCl and HNO₃ leaching, and Al–V [11], –Ce [12], –Nb [13], and –AlFeNiCr [14] alloys, and X-ray diffraction spectra before (b) and after (c) HCl and HNO₃ leaching for Si–7.5 at.% Al–7.5 at.% V.

Electrical resistances of the Si–Al–V alloys before and after de-alloying were measured at room temperature using a four-terminal measuring method with electrode distances of 2–20 mm. Capacitances were calculated as a function of frequency between 1 mHz and 1 MHz from electric charge/discharge pulse curves of 10 V applied at 25 ns–100 ms intervals, using a mixed-signal oscilloscope (MSO 5104, Tektronix, OR, USA) and 30 MHz multifunction generator (WF1973, NF Co., Yokohama, Japan) on the basis of simple exponential transient analysis.

3. Results and discussions

To select alloys with charging/discharging abilities suitable for electric storage capacitors, we measured the electrical resistivity at room temperature of the Si–(Al + V) alloys before and after acid leaching. The results are shown in Fig. 1a, along with reference data for Si–V [11], –Ce [12], –Nb [13], and –AlFeNiCr [14] alloys. The observed resistivity change of the Si–(Al + V) alloys before acid

leaching is fairly consistent with that reported for Si–V, –Ce, –Nb, and –AlFeNiCr alloys. The resistivity of the de-alloyed samples decreased from 10^9 to $10^4 \mu\Omega\text{cm}$, values 10^{-2} – 10^{-7} lower than that of Si ($2 \times 10^{11} \mu\Omega\text{cm}$) with increasing (Al + V) content. In anticipation of the higher resistivity required for prompt discharging, we selected the Si–7.5 at.% Al–7.5 at.% V sample as the representative specimen in this study. Fig. 1b and c shows XRD spectra of the specimens before and after de-alloying, respectively. Before de-alloying, the sample consists of a mixture of crystalline Si, Al, VSi₂, Si₂V, and Al₂O₃, while after de-alloying the sample exhibited polycrystalline Si, also with low Al₂O₃ content.

We then measured voltage transient phenomena as a function of time for charging and discharging in input and output circuits at 1 kHz. The results are presented at Fig. 2a and b. Transient analysis of Fig. 2a and b gave capacitance values of 77 and 111 pF for

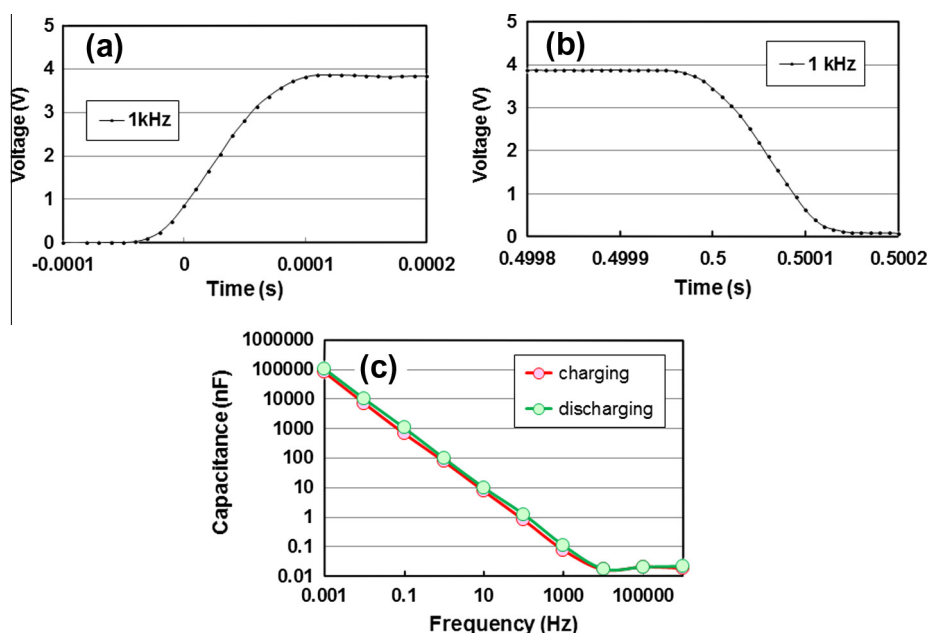


Fig. 2. (a and b) Voltage transient curves for charging and discharging in the input and output circuits at 0.1 Hz. (c) Frequency dependence of capacitance for Si–15, –20, –30, –40 at.%(Al + V).

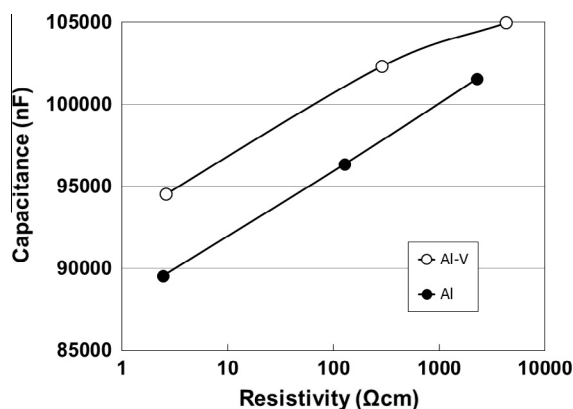


Fig. 3. Relation between capacitance and resistivity for de-alloyed Si-Al-V and Si-Al specimens.

charging and discharging, respectively. Capacitance as a function of frequency for this sample is presented logarithmically in Fig. 2c. All capacitances decreased parabolically to 18 pF with increasing frequency up to 10 kHz, before becoming saturated in the frequency region 10 kHz–1 MHz. The alloy showed a maximum capacitance of 105 μ F for discharging at 1 mHz, being almost the same as de-alloyed Si-Al alloys. This behavior implies ac current charging/discharging, with the observed decrease in capacitance derived from dielectric interfacial dispersion at higher frequencies.

As can be seen from the resistivity in Fig. 1a and capacitance in Fig. 2c, the capacitance is associated with resistivity of de-alloyed specimens after leaching. The effect of the resistivity on the capacitance of the de-alloyed Si-7.5 at.%Al-7.5 at.%V, -10 at.%Al-10 at.%V, and -15 at.%Al-15 at.%V specimens is presented in Fig. 3, along with those of the Si-20 at.%Al, -30 at.%Al, and -40 at.%Al specimens [7]. Capacitance increases with increasing resistivity. This suggests higher capacitance needs for higher resistivity. Furthermore, the addition of V enhances the capacitance for the de-alloyed Si-Al specimens.

Since it is considered that de-alloyed Si-(Al + V) is organized as a complex circuit of an m -rank parallel and n -row series combination of femtofarad Si capacitors, as is the case for Si-Al [7] alloys and Ni-Nb-Zr-H glassy alloys [2], we measured the electrode distance dependence on discharging capacitance for the de-alloyed specimen. As can be seen from Fig. 4a, the capacitance C for all frequencies increased linearly with electrode distance d . At 0.1 Hz, $C = 3.06d + 969.7$ (Fig. 4b), suggesting an existence of parallel circuits in the alloy. However, if a perfect parallel combination existed, the capacitance would be expressed by $C = 254.8d$ and the alloy would be composed of distributed constant equivalent circuits of series C with 1.2% parallel C (Fig. 4c). Fig. 4d presents the surface microstructure of the de-alloyed specimen prepared in HCl and HNO₃ solutions, showing Si grains with narrow canyons which store electric charge. Although an investigation of the three-dimensional cluster configuration is indispensable to the construction of giant capacitance, it was very difficult to determine the actual canyon structure because of its brittleness. Further precise observation is called for. Since large electric storage could be obtained by the parallel combination network of huge numbers of atomic-size spaces, further improvements are also required such as supercooling through higher roller speeds [5] and hydrogen penetration [1–4] for construction of surface structures with a higher density of extremely narrow canyons.

4. Conclusion

To improve the capacitance of de-alloyed Si-Al alloys, the frequency dependent capacitance of de-alloyed Si_{1-x}(Al_{0.5}V_{0.5})_x ($x = 0.15, 0.2, 0.3$, and 0.4) alloy ribbons was measured between 1 mHz and 1 MHz at room temperature, using exponential transient analysis for electric charging/discharging. The de-alloyed specimens showed resistivities from 0.01–4300 Ω cm, values 10^{-2} – 10^{-7} lower than that of Si (2×10^{11} $\mu\Omega$ cm) with increasing (Al + V) content. The Si-7.5 at.% Al-7.5 at.% V alloy ribbon showed

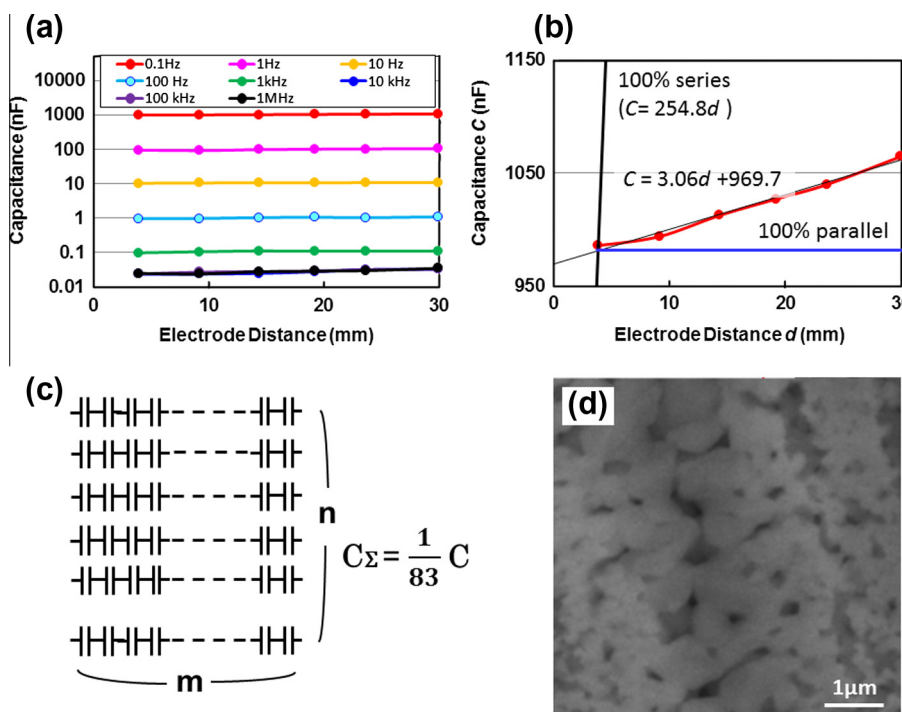


Fig. 4. (a and b) Electrode distance dependence of capacitance. (c) Complex circuit of m -rank parallel and n -row series combination in glassy alloys. (d) SEM image of de-alloyed Si-7.5 at.% Al-7.5 at.% V alloy.

maximum capacitance of 105 μF for discharging at 1 mHz. All capacitances decreased parabolically with increasing frequency up to 10 kHz, before becoming saturated in the frequency region 10 kHz to 1 MHz. In comparison with de-alloyed Si–Al and Si–Al–V specimens, the addition of V enhances the capacitance. A higher capacitance requires a higher resistivity of the de-alloyed specimens. From the electrode distance dependency for the capacitance, the alloy would be composed of distributed constant equivalent circuits of series C with 1.2% parallel C. Thus this paper provides useful information for novel science and technologies associated with battery materials.

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