

# Fabrication and Electrochemical Characteristics of Crack-Resistant Si-Based Anode Materials for All-Solid-State Thin-Film Batteries

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A series of Si-Zr and Si-Zr-Ag films were prepared by the co-sputtering method to examine their microstructural stability and electrochemical performances. Si-Zr thin films like  $\text{Si}_{58}\text{Zr}_{42}$  and  $\text{Si}_{48}\text{Zr}_{52}$ , alloyed with significant proportions of Zr, show excellent cycle performance with no microstructural change to the film surfaces, although they exhibit a reduced reversible capacity. Si-Zr-Ag film shows a charge-discharge profile with a plateau-like region, in which the cycle performance and the morphological stability depend on film fabrication conditions such as the substrate and the applied bias voltage.

**Keywords:** all-solid-state thin film microbattery, Si-based anode, thin-film anode, microstructural stability

## 1. INTRODUCTION

Silicon-containing thin films are promising for anodes of thin-film rechargeable batteries because of their specific high capacity.<sup>[1-10]</sup> However, Si phase undergoes significant volume changes during Li insertion/extraction reactions, which causes mechanical cracking of the electrode film and poor cycle-life. Many attempts have been made to improve the cycle performance of Si thin film anodes. For example, the cycle performance of Si thin film electrodes has been significantly improved by appropriate surface roughening of the substrate, in which the Si thin film was separated into columns after the first cycling.<sup>[11,12]</sup>

However, it should be noted that when Si thin film is used as the anode for all-solid-state thin film batteries, the mechanical cracking that occurs during charge-discharge (Li insertion-extraction) cycling has a detrimental effect on the interface stability between the Si anode and electrolyte films, so that the properties of the thin film batteries are degraded. Hence, for the fabrication of all-solid-state thin film batteries, Si-based anodes should be resistant to mechanical cracking during charge-discharge cycling. However, little attention has been given to the mechanical cracking behavior of those Si-based anode films during cycling.

In this work, alloy compositions and film fabrication conditions have been examined to allow production of highly crack-resistant Si-based anode films.

## 2. EXPERIMENTAL PROCEDURE

Si-Zr and Si-Zr-Ag thin films were deposited on a Cu sub-

strate by co-sputtering of separate pure elemental targets using the magnetron sputtering method. For Si-Zr-Ag alloy, a D. C. negative substrate bias of -50 V was applied, and a Ni substrate was used for comparison with samples deposited on a Cu substrate. The base pressure was  $2 \times 10^{-6}$  Torr. Argon pressure during deposition was  $5 \times 10^{-3}$  Torr. The film thickness was about 200 nm.

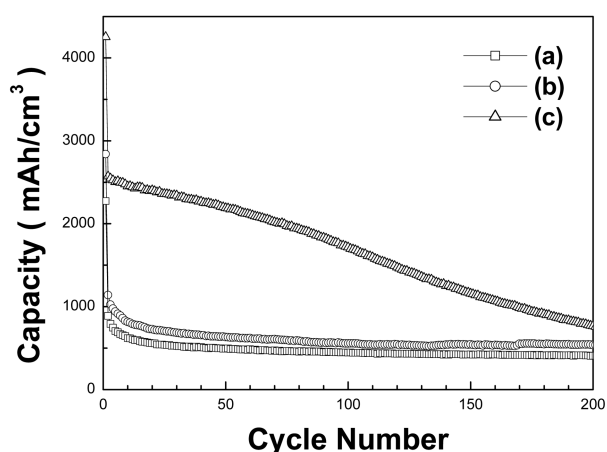
Composition analysis for the films was carried out by energy-dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). The surface morphology was observed by field-emission scanning electron microscopy (FESEM).

Electrochemical measurements were performed in 2016 coin type half-cells using metallic lithium for both the reference and counter electrodes. The electrolyte was a 1M  $\text{LiPF}_6$  dissolved in a 50 : 50 (vol. %) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), provided by Techno Semichem Co., Ltd, Korea. All cells were galvanostatically tested at 30°C between 0 and 1.5 V vs.  $\text{Li/Li}^+$ .

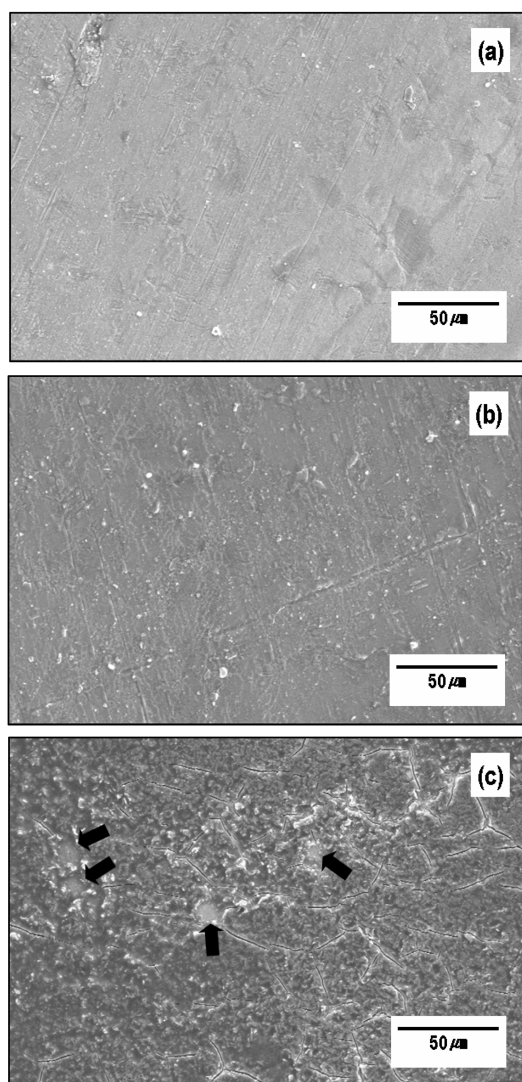
## 3. RESULTS AND DISCUSSION

Figure 1 shows the cycle performance of the Si-Zr thin film electrodes. The cycle performance was improved by alloying with Zr. This improvement is attributed to the strong bonding of Zr atoms with Si atoms, which prevents Si from alloying with a large amount of Li.<sup>[7]</sup> Notably, the  $\text{Si}_{58}\text{Zr}_{42}$  and  $\text{Si}_{48}\text{Zr}_{52}$  thin films show no capacity fading for over 200 cycles. The electrochemical cycling characteristics of the Si-based thin film electrodes are closely related with the changes in the morphology of the film electrodes during cycling. The SEM surface images of the Si-Zr thin film electrodes observed after 200 cycles are shown in Fig. 2. The

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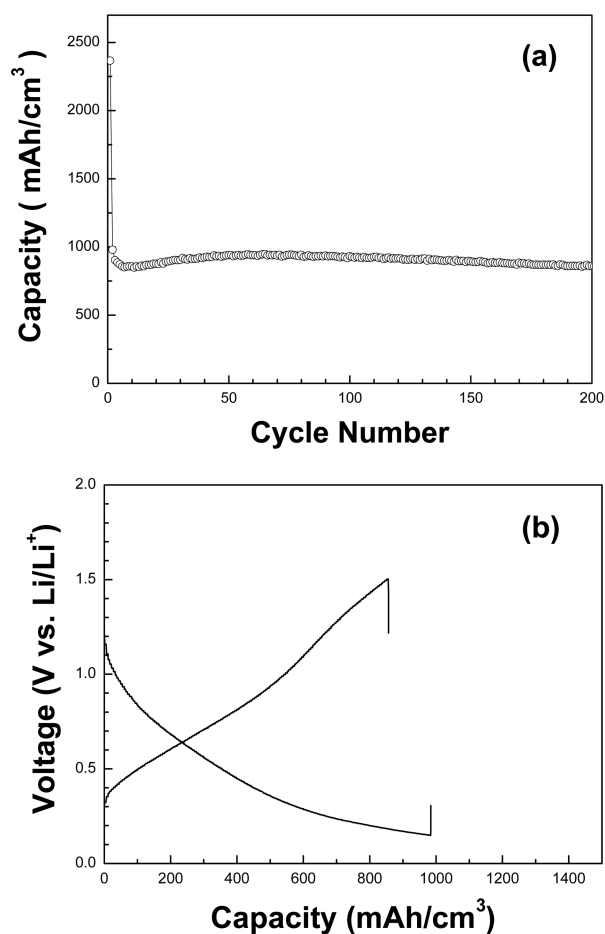
**Fig. 1.** Charge capacity vs. cycle number of the Si-Zr thin films: (a)  $\text{Si}_{48}\text{Zr}_{52}$ , (b)  $\text{Si}_{58}\text{Zr}_{42}$ , and (c)  $\text{Si}_{68}\text{Zr}_{32}$ .



**Fig. 2.** FESEM images of the Si-Zr thin films after 200 cycles: (a)  $\text{Si}_{48}\text{Zr}_{52}$ , (b)  $\text{Si}_{58}\text{Zr}_{42}$ , and (c)  $\text{Si}_{68}\text{Zr}_{32}$ .

$\text{Si}_{58}\text{Zr}_{42}$  and  $\text{Si}_{48}\text{Zr}_{52}$  films are devoid of any cracks and the surface morphology remains the same as in the images of the surface profiles of the Cu substrate. On the other hand, the surface of the  $\text{Si}_{68}\text{Zr}_{32}$  film shows cracks, and the film is detached from the Cu substrate in local regions (as indicated by arrows), which results in a loss of capacity.

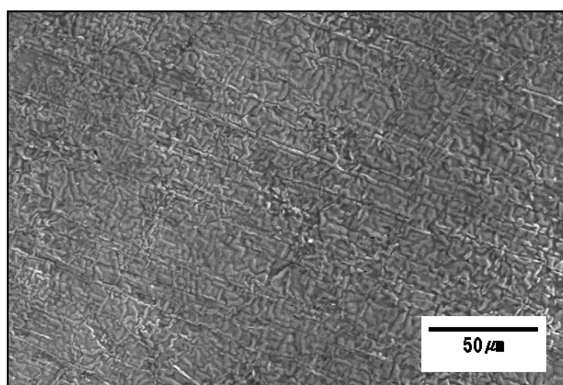
For all-solid-state thin film batteries, crack formation in the anode during cycling should be suppressed, thereby stabilizing the interface between the anode and electrolyte films. The morphological stability of Si-rich alloy films like  $\text{Si}_{68}\text{Zr}_{32}$  can be improved by shifting the lower cutoff voltage to a higher potential to induce smaller volume changes of the active Si phase. When the charge-discharge potential range is shifted from 1.5/0.0 to 1.5/0.15 V, the  $\text{Si}_{68}\text{Zr}_{32}$  anode displays excellent capacity retention, while it leads to a significant capacity reduction, as shown in Fig. 3(a). The corresponding charge-discharge curve for the 2<sup>nd</sup> cycle is presented in Fig. 3(b). Figure 4 shows an SEM image of the  $\text{Si}_{68}\text{Zr}_{32}$  film electrode after 200 cycles in the range of 0.15 to 1.5 V. As expected, there are no cracks even after 200 cycles, although the surface mor-



**Fig. 3.** Electrochemical characteristics of the  $\text{Si}_{68}\text{Zr}_{32}$  Sample applied to 0.15 to 1.5 V cutoff voltage: (a) Charge capacity vs. cycle number and (b) Charge-discharge curve for 2<sup>nd</sup> cycle.

phology does seem to be slightly changed.

On the other hand, anodes made of alternatives to metallic lithium can be also required to have a wide potential plateau at low potentials. It has been reported that the addition of Ag to Si-Zr systems leads to a charge-discharge curve with a plateau-like region and a higher capacity.<sup>[13]</sup> This is attributed to the formation of Zr-Ag bonds in the Si-Zr-Ag films, leading to the formation of a Si phase. It is expected, moreover,



**Fig. 4.** FESEM image after 200 cycles of the Si<sub>68</sub>Zr<sub>32</sub> Sample applied to 0.15 to 1.5 V cutoff voltage.

that the Zr-Ag bonds may act as a buffer for the volume change of the active Si phase.

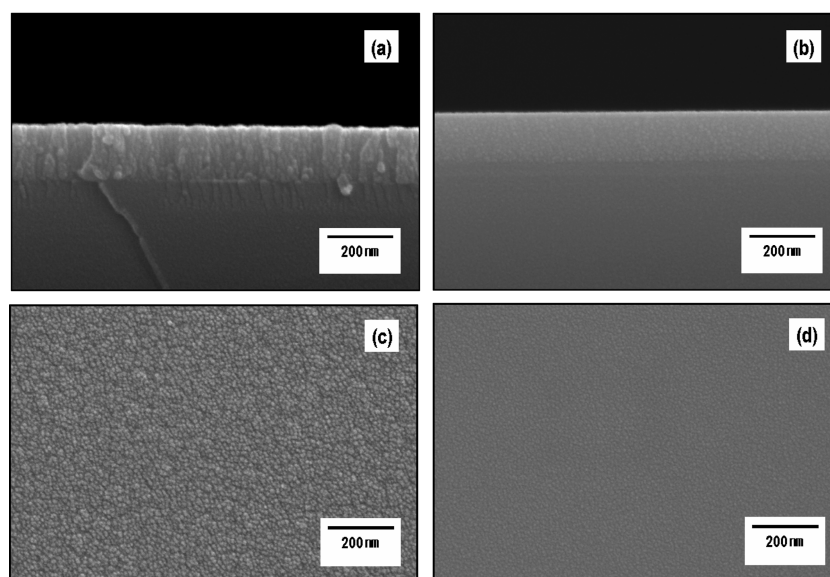
It is known that the structural properties of thin films prepared by magnetron sputtering can be modified and controlled from in situ substrate treatment like D. C. “bias,” and that the electrochemical performance of a vacuum-deposited Si-based film can be affected by the substrate used.<sup>[7,13]</sup> Consequently, three Si-Zr-Ag thin films were prepared for this experiment using different deposition conditions and substrates, as illustrated in Table 1.

Figure 5 shows a cross-sectional and a plane view of the Si-Zr-Ag thin films deposited with and without DC bias. The biased film is dense and has a smooth morphology. Figure 6 shows the cycle performance of the Si-Zr-Ag film electrodes. The biased film electrode deposited on a Ni substrate exhibits a distinctly stable cyclability. It appears that the cycling behavior is closely related to the morphological degradation behavior of the film electrodes during cycling (Fig. 7).

For the unbiased film on a Cu substrate (sample A), a delamination of active material from the substrate leads to a loss of electronic contact between the active material and the current collector. The adhesion between the film electrode and substrate is improved by a negative bias voltage applied

**Table 1.** The specification of the Si-Zr-Ag thin films

Sample	Substrate	Atomic concentration			DC bias treatment
		Si	Zr	Ag	
A	Cu	60	24	16	×
B	Cu	60	24	16	O
C	Ni	60	24	16	O



**Fig. 5.** FESEM images of Si-Zr-Ag thin films deposited with/without DC bias treatment during deposition: (a) Cross-sectional image without DC bias treatment, (b) Cross-sectional image with DC bias treatment, (c) Plane view image without DC bias treatment, and (d) Plane view image with DC bias treatment.

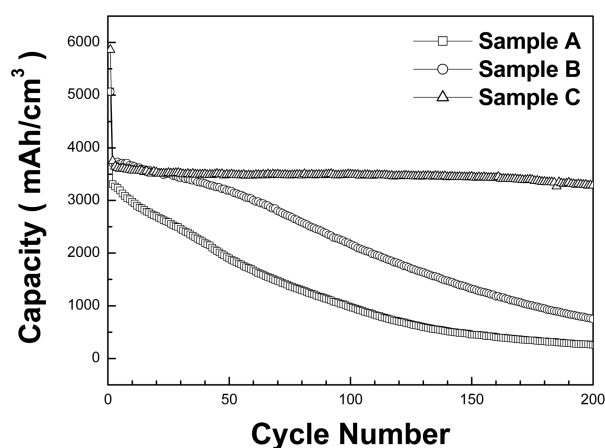


Fig. 6. Charge capacity vs. cycle number of the Si-Zr-Ag samples described in Table 1.

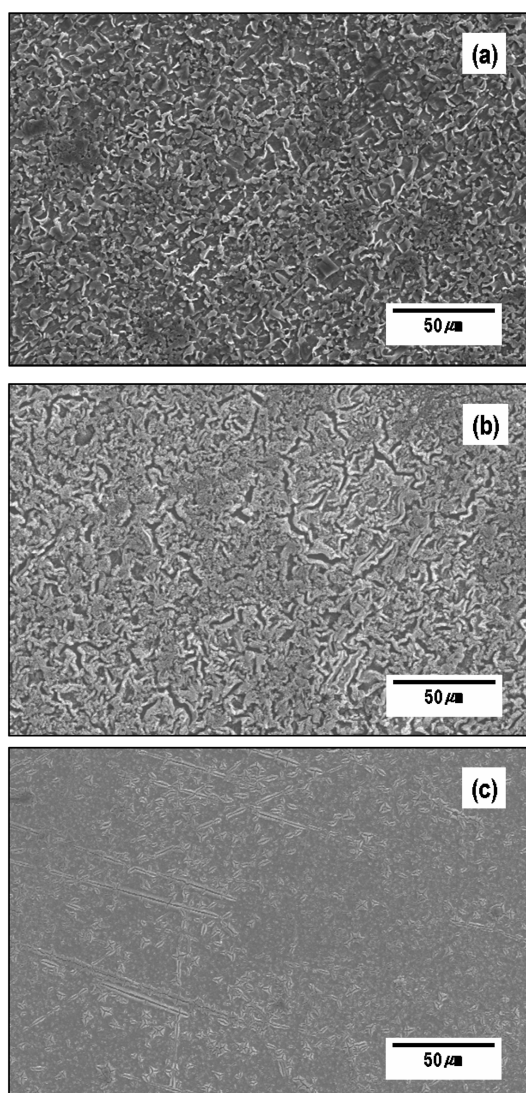


Fig. 7. FESEM images of the Si-Zr-Ag samples after 200 cycles: (a) sample A, (b) sample B, and (c) sample C.

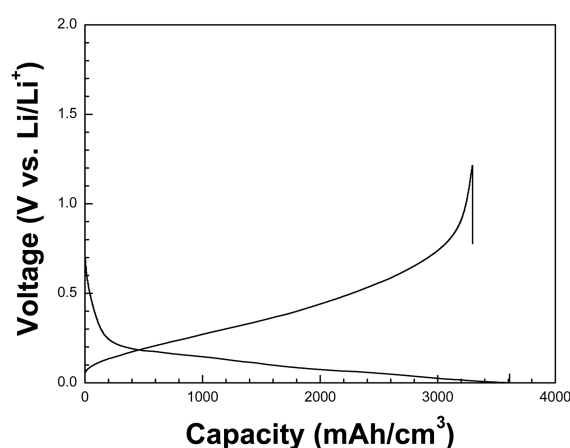


Fig. 8. Charge-discharge curves of the sample C for 2nd cycle.

to the substrate during deposition, and more significantly enhanced by using a Ni substrate instead of a Cu substrate. In particular, for the biased film on Ni, no continuous crack network is observed even after 200 cycles, although fine localized cracks do appear. The enhanced adhesion on the Ni substrate is presumably because the Si-Ni system has a large negative value for the enthalpy of formation compared with the Si-Cu system. The large negative heat of mixing indicates the strong chemical affinity between constituent elements. It is expected that a crack-free, stable Si-Zr-Ag film electrode can be obtained by further optimizing the film composition and deposition conditions. The Si-Zr-Ag film electrode (sample C) shows a charge-discharge curve with a plateau-like region and a large reversible capacity (Fig. 8).

#### 4. CONCLUSIONS

The electrochemical properties and microstructural stability of a series of Si-Zr and Si-Zr-Ag films have been investigated. Si-Zr thin film electrodes such as  $\text{Si}_{58}\text{Zr}_{42}$  and  $\text{Si}_{48}\text{Zr}_{52}$  show excellent cycle performance and are devoid of any cracks even after 200 cycles, although they do show reduced capacities and sloping charge-discharge curves as a result of alloying with significant proportions of Zr.

The introduction of Ag to the Si-Zr system changes the charge-discharge curve from a sloping profile to a profile with a plateau-like region, which leads to an increased reversible capacity. The cycle performance and microstructural stability of the Si-Zr-Ag film are improved by applying a negative bias voltage during deposition. A further improvement has been achieved by using Ni instead of Cu as a substrate. This is attributable to the enhanced adhesion of the film electrode to the substrate.

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