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Letter

Electrochemical and mechanical properties of superelastic electrode consisting of Ti substitute $LiNiO_2$ film on Ti–50Ni alloy

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ABSTRACT

By annealing Ni film/Li film/Ti–50Ni alloy in O_2 atmosphere, we fabricated a superelastic electrode consisting Ti–$LiNiO_2$ film as a cathode material and TiNi substrate as a current collector. The electrode with partial shape memory effect and superelasticity exhibited a high operating voltage of 3.7 V and a good reversibility of Li ion. An increased M_S of TiNi alloy in the electrode was attributed to a compressive stress imposed by TiO_2 and $Li_{0.98}\,Ni_{0.7}Ti_{0.3}O_{1.92}$ layers.

1. Introduction

Recently flexible electronic devices such as display, flexible electronic paper (E-paper) and flexible keyboard have been developed for next generation personal computers (PCs). Those devices essentially require flexible power sources (batteries) that can be flexible together with them. Thin film battery is usually known to be geometrically proper to flexible batteries. Moreover, when current collectors with superelasticity are applied to the thin film battery, the flexibility of battery will be improved significantly. Even though both Al and Cu are used as current collectors of cathodic–anodic electrodes in present Li batteries, they are not proper to a flexible battery because of their low elastic limits.

Ti–Ni alloys possess the shape memory effect and the superelasticity generated by the thermo-elastic martensitic transformation [1], and are widely used as thermal actuators due to those properties. Beside the application of actuator, the alloy with Ti and Ni elements can be used as a source material for an integrated electrode of Li batteries. In previous work [2], NiS_2 electrode that consists of metal sulfide at the surface as the cathode and TiNi alloy as a current collector could be obtained by sulfidation of TiNi alloy.

$LiNiO_2$ has been considered as a promising cathode material for high energy rechargeable lithium-ion batteries due to its low cost, high energy density and non-toxicity [3–7]. Nevertheless, both the composition control for good electrochemical properties and the improvement of thermal safety still remained as main problems to overcome for its commercialization. Owing to the same reason, realization of film-type $LiNiO_2$ was difficult in physical vapor deposition (PVD) process. This may be due to the difficulties of fabricating an active $LiNiO_2$ thin film and achieving a target with the stoichiometric composition [8].

According to previous reports [9–11], x in $Li_{1-x}Ni_{1+x}O_2$ has to be minimized to obtain acceptable electrochemical properties and the substitution of the Ni ion is recommended to improve the thermal safety. In particular, the substitution by Ti ions could obtain both overall electronic neutrality and structural integrity, and the Ti substituted $LiNiO_2$ (Ti–$LiNiO_2$) showed enhanced thermal stability and good electrochemical properties [12].

On this basis, we fabricated a superelastic electrode consisting Ti–$LiNiO_2$ film as a cathode material and TiNi substrate as a current collector. For this, thermal synthesis of Ni/Li/TiNi system was performed in O_2 atmosphere. Here, Ni film without activation for Li was used as a capping layer to protect from oxidation.

In this work, the formation of Ti–$LiNiO_2$ fabricated by the thermal synthesis of Ni/Li/TiNi specimen is confirmed by investigating structural and electrochemical properties. The flexibility of the electrode was indirectly evaluated by characterizing mechanical properties including transformation behavior, superelasticity and shape memory effect.

2. Experimental procedure

A Ti–50Ni (at%) alloy ingot was prepared by vacuum induction melting. Plate-type alloys were obtained from the ingot. In order to prepare a substrate, the TiNi plates were worked into sheets (thickness: 0.5 mm) by hot-rolling at 1123 K. The solution treatment of the fabricated TiNi sheets was performed at 1123 K.

Li and Ni films were deposited in order on a TiNi substrate by thin film processes. Thermal evaporation and DC magnetron sputtering were used to deposit Li and Ni

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films, respectively. The topmost Ni film is expected to restrain Li evaporation at high temperature and give a sufficient synthesis time. Since Ni is an inactive material for Li, preliminary samples can be fabricated without any compounds between Ni and Li. Thermal synthesis of Ni/Li/TiNi specimen was performed by annealing in the open quartz tube at 773–1083 K for 30 min, where the best electrochemical properties were obtained at 973 K. Gas mixed with Ar (200 SCCM) and O_2 (50 SCCM) was continuously flowed into the tube during the synthesis.

Cross-section of as-deposited and annealed Ni/Li/TiNi specimens was observed with field emission scanning electron microscopy (FE-SEM). Their crystallographic structures were investigated by means of X-ray diffraction (XRD) with a Cu-Kα □radiation. Electrochemical measurements were performed in CR2032 coin cells composed with an electrode consisting of Ti substitute $LiNiO_2$ cathode material and TiNi substrate. A counter electrode was used as a lithium metal foil. Electrolyte was 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The cells were assembled in an Ar-filled glove box. Galvanostatic charge–discharge tests were conducted between the initial OCV(open circuit voltage) and 4.5 V, and then between 4.5 and 2.5 V after the first cycle. The constant current of 0.3 mA was applied for the charge–discharge test.

Transformation behavior of specimens was investigated by differential scanning calorimetry (DSC) measurements with a cooling and heating rate of 0.17 K/s. The shape memory characteristics were investigated by thermal cycling tests under constant load with a cooling and heating rate of 0.017 K/s. Elongation on cooling and its recovery on heating were measured by linear variable differential transformer. The superelasticity was examined by tensile tests at various temperatures with a strain rate of 10^{-4}/s.

3. Results and discussion

Cross-sectional SEM images of as-deposited and annealed Ni/Li/TiNi specimens are shown in Fig. 1(a) and 1(b). A boundary between Li and Ni films can be seen in Fig. 1(a) and it is found that a Li film with a thickness of 40 μm is deposited on a Ti–50Ni substrate and a Ni film with a thickness of 10 μm is deposited on the Li film. After annealing at 973 K in O_2, the boundary disappears and a single film is formed on the TiNi substrate. The annealed film exhibits a decreased thickness (19 μm) compared to the as-deposited film, which is resulted from a thermal reaction among Li, Ti, Ni and O, and a partial vaporization of Li with the low melting temperature (453 K) during annealing procedure.

X-ray diffraction patterns of as-prepared and annealed specimens are shown in Fig. 1(c), where a standard pattern (JCPDS No. 871544) of Ti substituted $LiNiO_2$ ($Li_{0.98}$ $Ni_{0.7}Ti_{0.3}O_{1.92}$) is given for comparison. Form here, the Ti substituted $LiNiO_2$ is described as the Ti–$LiNiO_2$. Diffraction peaks of the Ni film and the B2 parent phase of Ti–50Ni substrate are found at the as-deposited film, while any peaks related to the Li film are not observed in spite of the formation of thick Li film. Thus the Li film deposited between Ni film and TiNi substrate is considered to be amorphous because of a rapid deposition rate of thermal evaporation. After annealing, Ti–$LiNiO_2$ peaks with high intensity appear together with weak peaks of the B2 phase and the TiO_2 phase. It is considered that the formation of Ti–$LiNiO_2$ is resulted from the reaction of lithium oxide with Ti and Ni in substrate, because Ti and Ni are inactive materials for Li.

In order to confirm the formation of Ti–$LiNiO_2$ cathode film, Li desertion/insertion (charge/discharge) behaviors in the film were investigated electrochemically. Change in voltage of a cell with the electrode corresponds to Li desertion/insertion process in only Ti–$LiNiO_2$ film. For five cycles, charge/discharge curves of the cell with the annealed specimen are given in Fig. 2, which shows voltage changes with the alternate charge/discharge process. It is found

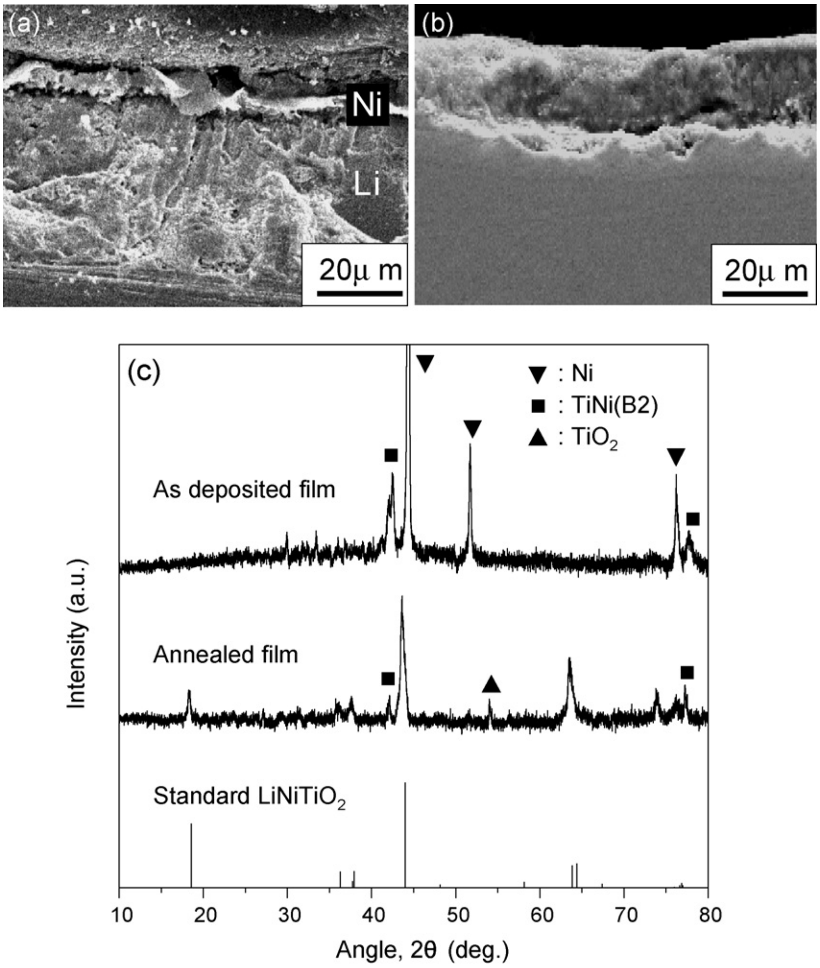

Fig. 1. Cross-sectional FE-SEM micrographs of (a) as-prepared Ni/Li/TiNi specimen and (b) annealed Ni/Li/Ti–50Ni specimen. (c) X-ray diffraction patterns of (a) and (b).

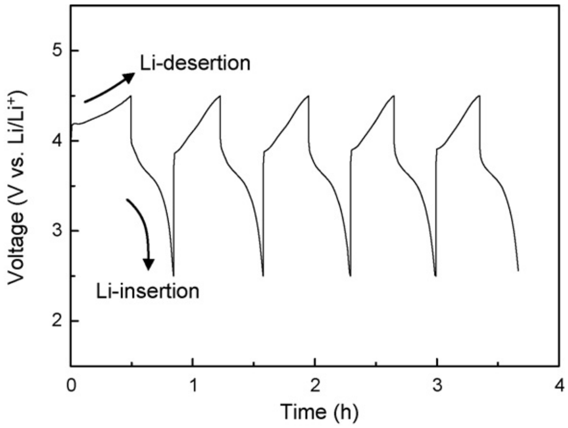

Fig. 2. Voltage vs. time curves of a cell with annealed Ni/Li/TiNi specimen, showing the cyclic Li desertion/insertion process.

that a Li ion transfer reversibly occurs at every cycle. In the annealed specimen, a flat voltage profile appears around 4.3 V at the first charge, while the voltage profile shifts toward lower voltage and reaction becomes stable after the second charge. This can be considered that Li desertion first occurs from Li_2O_2 and then from Ti–$LiNiO_2$, because charge voltage of Li_2O_2 is similar to the result (4.25 V) reported from composite electrodes of Li_2O_2 [13]. Thus it is believed that a small amount of Li_2O_2, which cannot be detected by XRD, exists on the surface of the annealed specimen. At a current density of 300 $\mu A/cm^2$, which is relatively high current for thin film electrode, the electrode showed good electrochemical properties including a high operating voltage of 3.7 V and the initial discharge capacity of 103 $\mu Ah/cm^2$, which is very effective to fabricate a thin film battery with a high power density.

Fig. 3(a) shows DSC curves of the annealed Ni/Li/Ti–50Ni specimen obtained between 200 and 400 K. One clear DSC peak corresponding to the B2-B19′ transformation appears on each cooling and heating curve. For comparison, DSC curve of a Ti–50Ni substrate is shown in Fig. 3(b). Comparing Figs. 3(a) and 3(b), it is found that M_S (the B2-B19′ transformation start temperature) increases by annealing. The volume change accompanied by the B2-B19′ transformation in TiNi alloys is known to be −0.526 % [14]. In fact, transformation temperatures of TiNi alloys were reported to increase by applying hydrostatic pressure [15,16]. When TiNi alloys are annealed in O_2, the oxide layers such as TiO_2 and Ti–$LiNiO_2$ formed on the surface is considered to impose a compressive stress to specimens because molar volume of a TiNi alloy increases by oxidation [17]. Therefore, the increase in M_S is attributed to a compressive stress induced by the oxide layers.

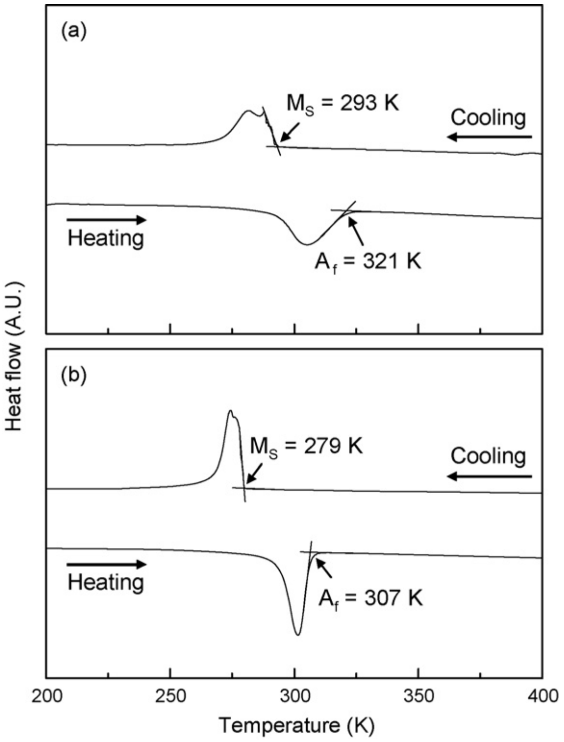

Fig. 3. DSC curves of (a) annealed Ni/Li/TiNi specimen and (b) TiNi alloy.

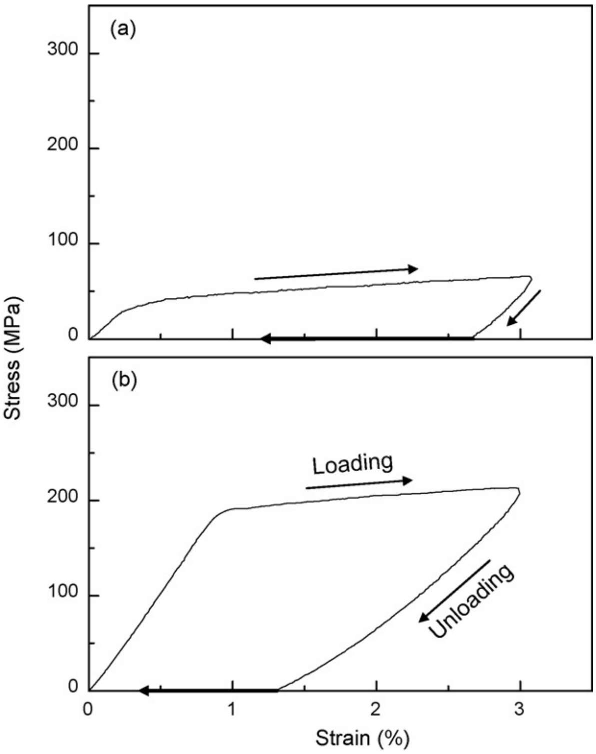

Fig. 4. Stress–strain curves of annealed Ni/Li/TiNi specimen at (a) 293 K (M_S) and (b) 321 K (A_f).

In order to investigate the shape memory effect and superelasticity of the annealed specimen, tensile tests were made at M_S and A_f (the B19′-B2 transformation finish temperature). Fig. 4 shows stress–strain curves obtained from tensile test. From Fig. 4(a), it is found that the shape memory effect appears at the specimen with Ti–$LiNiO_2$ film, although a part of strain developed on loading is not recovered on heating up to 373 K after unloading. This incomplete shape memory effect is resulted from the surface oxide layers which hinder the shape recovery of Ti–50Ni substrate. This implies that the cathode layer does is well adhered to the TiNi substrate, though cracks are generated in the thin film. From Fig. 4(b), it is found that the specimen shows only the partial superelasticity with the superelastic recovery ration of 57 %. This partial superelasticity is ascribed to the facts that surface oxide layers hinder the shape recovery of Ti–50Ni substrate and that annealing temperature of 973 K for oxidation is somewhat high for obtaining good superelasticity.

4. Conclusions

A Ti substitute $LiNiO_2$ cathode film was successfully fabricated through a thermal synthesis of Ni/Li/Ti–50Ni bi-layered specimen. The electrode exhibited a high operating voltage of 3.7 V and a good reversibility during Li insertion/desertion process. An increased M_S of TiNi alloy in the electrode was attributed to a compressive stress imposed on the alloy by TiO_2 and $Li_{0.98}$ $Ni_{0.7}Ti_{0.3}O_{1.92}$ oxide layers. The electrode partially exhibited the shape memory effect and the superelasticity despite of the oxide layers.

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