

The Effects of Cu-doping in V_2O_5 Thin Film Cathode for Microbattery

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Abstract—Copper-doped vanadium oxide ($Cu_xV_2O_5$) thin film cathode materials for a thin film microbattery have been prepared by DC reactive magnetron co-sputtering with O_2/Ar ratio of 10/90 and compared with pure V_2O_5 thin film. The film structures have been characterized by x-ray diffraction analysis, transmission electron microscopy, Auger electron spectroscopy and X-ray photoelectron spectroscopy. X-ray diffraction and TEM studies show that the $Cu_xV_2O_5$ film was amorphous and phenomenal behavior of copper present in thin film with substrate has been explained by thermodynamical model. Copper doping helps to increase the thickness of the film more than 1 micrometer resulting increase of total capacity. Cycling behavior of the $Cu_xV_2O_5/Lipon/Li$ configuration cell system was beyond 500 cycles with average capacity of $50 \mu Ah/cm^2\text{-}\mu m$, which is higher than the pure V_2O_5 thin film system.

Key words: Microbattery, Copper-Vanadium Oxide, Lithium Batteries, All-Solid-State, Thin Film Batteries

INTRODUCTION

With the advanced development in micro-processing and material science, electronic devices were miniaturized, resulting in low current consumption. However, the development of these device systems has more technical problems than a conventional device. One of the most important things is the fabrication of a small-sized power source to operate devices, according to reduction of device size. That is, a small or micro size power source is necessary to operate very small electronic devices. For example, a thin film microbattery fabricated directly onto a semiconductor chip package can save 100 to 1,000 times the volume required by conventional coin cells. Therefore, it is a promising alternative micro power source, since the typical thin film process can miniaturize it. The microbattery not only has high energy and power densities, but also can be fabricated in arbitrary shapes and any required size to satisfy specific requirements. In addition, it does not have aqueous electrolytes, which forms dendrite phases during charge-discharge processes, resulting in high cycle performance after cycling thousands of times. All-solid-state microbatteries have the advantages of low self-discharge, high stability, broad working temperature range, and the easy fabrication of designed forms, which could be applied to contactless smart card, medical and health care, and microelectromechanical system (MEMS) [Bates et al., 1993]. Amorphous vanadium oxide has been recognized as a promising cathode material for thin film lithium secondary batteries or electrochromic devices due to their high insertion of the lithium ions over the crystalline forms [Passerini et al., 1997; Le et al., 1995, 1996; Lim et al., 2000;

Jeon et al., 1999]. Shimizu et al. [1993] reported that the cycling performance of the crystalline V_2O_5 appears to be irreversible when discharged below 2.3 V vs. Li^+ , corresponding to an intercalated lithium amount of $x \approx 1$ in $Li_xV_2O_5$. McGraw et al. [1998] reported that the amorphous films grown by both pulsed laser deposition (PLD) and plasma enhanced chemical vapor deposition (PECVD) exhibited excellent capacity and stability over extended number of cycles. West et al. [1993] reported that the vanadium oxide xerogels appear to be good alternatives to sputtered films, although the capacity for Li insertion is lower. Recently, Coustier et al. [1997, 1999] reported that the xerogel films or aerogel-like powders showed highly reversible Li^+ intercalation with addition of some metals, such as copper and silver. Also, they proved that the amorphous forms of vanadium bronzes had high electronic conductivity and the porous structure was needed to reduce the diffusion limitation upon lithium insertion. All-solid-state lithium batteries based on V_2O_5 thin films for both electrodes were fabricated by Baba et al. [1999] by using the solid electrolyte as lithium phosphorous oxy nitride (Lipon). Jeon et al. [2000] showed that the capacity of the in-situ sputtered $V_2O_5/Lipon/Li$ cell was higher due to reduction in interfacial resistance between electrode and solid electrolyte. Although, Lim et al. [2000] already reported that the amorphous vanadium oxide was appropriate cathode material in a room temperature process, it was hard to grow film thickness above $4,000 \text{ \AA}$ to increase the total capacity. In this work, Cu-doped vanadium oxide thin film cathode for all-solid-state lithium rechargeable microbattery was fabricated to increase film thickness above $1 \mu m$ by a DC reactive magnetron co-sputtering. Although, Coustier et al. [1997, 1999] already reported the copper and silver effects in V_2O_5 , it exists in metallic state and different from our experiments. In addition, copper distribution in a vanadium oxide thin film was investigated from thermodynamical point of view. Characteristics of a sputter-deposited thin film $Cu_xV_2O_5$ electrode of reversible capacity and cycle performance are described. A better understanding of the film

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structure, film morphology and the electrochemical behavior is pursued. Characterization of all-solid-state microbattery was considered by sequential Lipon solid electrolyte and lithium thin film deposition. $\text{Cu}_x\text{V}_2\text{O}_5$ thin film cathodes showed higher capacity and cycle life, which proves that the Cu-doped V_2O_5 thin film could be good alternatives to the pure vanadium oxide films.

EXPERIMENTAL

Cu-doped vanadium oxide thin films were prepared by DC reactive magnetron co-sputtering on stainless steel current collector, which was coated on coming glass substrate at room temperature. The base pressure was 5×10^{-6} Torr. The deposition pressure of argon and oxygen mixtures during deposition was maintained at 8×10^{-3} Torr, while the O_2/Ar ratio was 10/90 and total gas flow rate was 14 sccm. To minimize the poisoning effect of the metal target surface, oxygen gas inlet was connected through the ring type tube closed to the substrate. The substrate was rotated at 10 rpm to improve the film uniformity. Before deposition, pre-sputtering was carried out under argon atmosphere for 20 min with 4-inch vanadium (Pure Tech.) and copper (Cerac) target. A schematic diagram of the experimental apparatus is shown in Fig. 1. Film morphology and thickness were determined by field emission scanning electron microscopy (FE-SEM Hitachi S-4100). The structures of the films deposited at room temperatures were analyzed by X-ray diffraction analysis using $\text{Cu K}\alpha$ radiation (XRD, Rigaku). Auger electron spectroscopy (AES, Perkin Elmer PHI-670), X-ray photoelectron spectroscopy (XPS) was used to compare the vanadium, oxygen and copper contents from the as-deposited thin films. For the preliminary tests of cathode material, cells were assembled with lithium foils (Cyprus) as the counter and reference electrodes and 1 M LiPF_6 in EC : DMC (1 : 1, Merck) electrolytic solution. Separators were polyethylene-based membrane (Ube). All cells were assembled in the dry-room below -65.5°C of the dew point. Lipon thin film solid electrolytes were deposited on Cu-doped vanadium oxide thin film at room temperature by RF magnetron sputtering of a Li_3PO_4 target

under nitrogen atmosphere. Target was fabricated by lithium phosphate power (Aldrich, 99.9%). Powder was ball-milled for 24 hours after calcination at 850°C . Pressed target at 100 kgf/cm^2 in addition of 5 wt% PVA binder was sintered at 950°C for 3 hours. In spite of sputtering in pure nitrogen, the surface of the Li_3PO_4 target became dark black and seemed to be nitrided. For the AC impedance measurements ss/Lipon/ss (ss : stainless steel) sandwich structure were fabricated on coming glass substrate with a Lipon thickness of $1.4\text{ }\mu\text{m}$ and a junction area of $1.2 \times 1.2\text{ cm}^2$. The thickness of the Lipon film was greater than the $1.2\text{ }\mu\text{m}$ to avoid shorting between the two current collectors. To measure the stability window with lithium metal contact, lithium metal was deposited by thermal evaporation equipment in a dry-room. All-solid-state thin film microbattery was fabricated by thermal deposition of lithium metal onto solid electrolyte as an anode. The total thickness of the cell was less than $6\text{ }\mu\text{m}$ and the cells were gold coated for the protection to air and also used as a current collector. Constant current galvanostatic charge/discharge tests were performed (Wonatech, WBCS 3000).

RESULTS AND DISCUSSION

Film surface was relatively smooth and adhered to the stainless steel substrate tightly based on a tape test.

Fig. 2 shows the XRD pattern of the as-deposited thin film. No crystalline peaks of the vanadium oxide were shown. The sharp peak at 44° represents the stainless steel (ss) substrate, and it is estimated that this thin film has the amorphous Cu-doped vanadium oxide phase. The amorphous structure was also confirmed by TEM. These properties are a result of ion-bombardment induced surface mobility of deposited atoms on the substrate. In general, it is known that the crystallites grow perpendicular to the substrate plane without significant voids for the effect of self-bias in the case of RF than the DC reactive sputtering. Actually, it was difficult to obtain a complete amorphous phase thin film when the RF power was applied in the oxygen inlet condition. However, the amorphous Cu-doped thin film could be easily obtained with high deposition rate by using DC reactive magnetron sputtering.

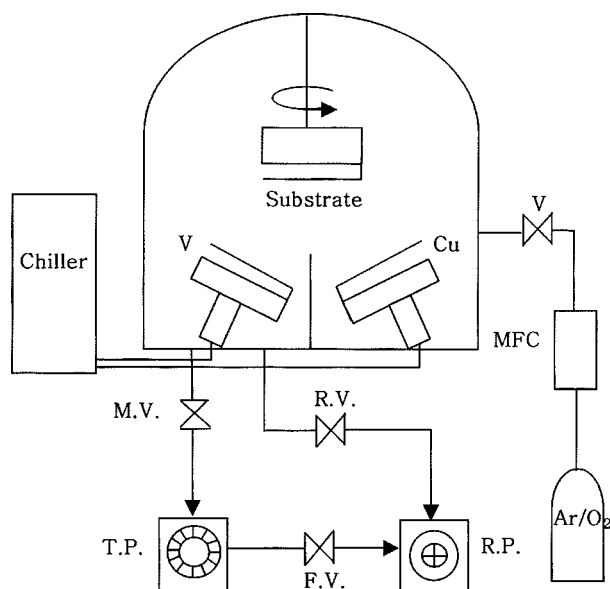


Fig. 1. Schematic diagram of co-sputtering system.

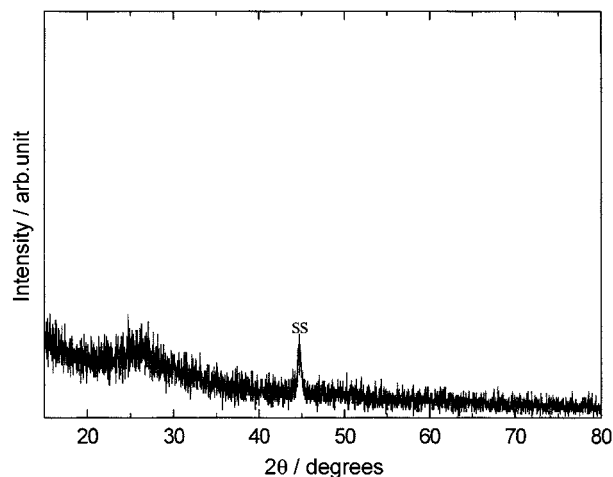


Fig. 2. X-ray diffraction pattern of the $\text{Cu}_x\text{V}_2\text{O}_5$ thin film. ss : stainless steel substrate.

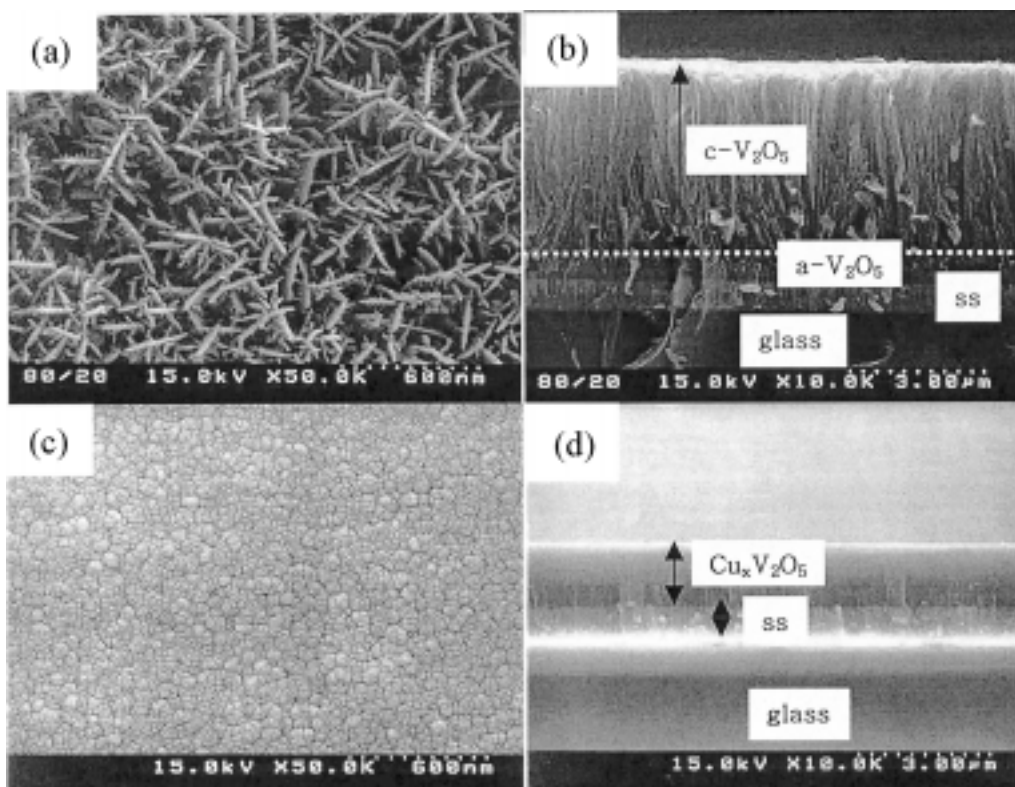


Fig. 3. Scanning electron micrographs of the surface and cross-sectional (a), (b) V_2O_5 and (c), (d) $Cu_xV_2O_5$ thin film.

Fig. 3 compares surface and cross-sectional SEM images of pure V_2O_5 and Cu-doped V_2O_5 thin film. It was observed that the fibrous crystalline film with porous surface grow rapidly after 4,000 Å, while the amorphous structure could be deposited to only 4,000 Å in pure V_2O_5 thin film as shown in Fig. 3(a) and (b). It is difficult to clarify which region is amorphous or crystalline by SEM. Thus, we used the TEM analysis and proved the above SEM images. Such phenomena could be described as target poisoning effect on reactive sputtering as a result of gradual oxidation of vanadium target surface under the oxygen atmosphere. That is, oxidation of target surface caused the loss in sputtering rate, resulting in increasing rearrangement probability of ad-atoms on the substrate and then crystalline nucleation occurred. These nuclei could grow easily, making hard to grow amorphous V_2O_5 thin film thicker than 4,000 Å. It made the total storage of charge and energy limited. However, Cu addition to V_2O_5 improved the growth of amorphous thin film, and the surface is relatively smooth and highly uniform, which shows the 30-50 nm wide grains as shown in Fig. 3(c) and (d). We could increase the total thickness up to 1.4 μm without any crystalline growth. It was supposed that sputtered Cu played a role of an additional getter pump for excess oxygen, so the thickness of amorphous $Cu_xV_2O_5$ thin film could be increased above 1 μm by adding Cu into V_2O_5 . Such features make the total discharge capacity higher than that of pure V_2O_5 . Also, the surface control in thin film battery is very important, because the surface roughness increases; the poor contact between the solid electrolyte and anode could cause the short problems as well as current concentration on the spot of the high energy density. Cu-doped vanadium oxide thin film and good adhesion to the stainless steel substrate (6,000 Å).

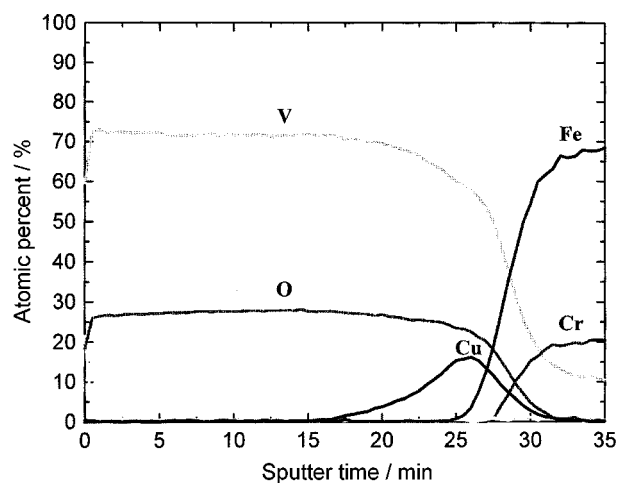


Fig. 4. Auger electron spectroscopy depth profiles of the $Cu_xV_2O_5$ thin film.

Fig. 4 shows the AES depth profile of the as-deposited Cu-doped vanadium oxide thin film. It is confirmed that the vanadium and oxygen exist uniformly from the surface, and it could be estimated that the film consists of V_2O_5 , for which O/V ratio is close to 5/2 of atomic percent. The amount of doped copper was less than 1 atomic percent homogeneously toward the depth direction, while the copper content increased in the interface with the substrate. AES data confirmed that thin film consisted of V_2O_5 in the surface region through XPS analysis; the difference of binding energy between V 2p_{3/2} and V 2p_{1/2} was 7.5 eV, although we could not detect the copper

bonding state for low analysis depth of about 10–100 Å. Generally, the film surface has high surface energy compared to inner phase, and it could be explained that copper oxide diffuses into substrate to maintain stable energy state during deposition, for which vanadium atom has relatively higher oxygen bonding energy than Cu atom. This is due to decrease of film surface energy. Such phenomena could be explained by thermodynamical model in a binary system proposed by Overbury et al. [1975], Wen et al. [1979] and Burton et al. [1975].

A: Ideal solution

$$X_2^s/X_1^s = X_2^b/X_1^b \exp[(\sigma_1 - \sigma_2)a/RT]$$

Where, $X_i^{s(b)}$: atom fraction if I in the surface (or bulk)

$$a_i = (\partial A / \partial n_i^s)_{T, P, n_j, \sigma}; \text{ partial molar surface area of I species assuming } a_1 = a_2 = a$$

B. Regular solution

$$X_2^s/X_1^s = X_2^b/X_1^b \exp[(\sigma_1 - \sigma_2)a/RT] \exp[\{\Omega(l+m)\}/RT\{(X_1^b)^2 - (X_2^b)^2\} + \Omega/RT\{(X_2^s)^2 - (X_1^s)^2\}]$$

Where, l : fraction of nearest neighbors to atom in the plane

m : fraction of nearest neighbors below the layer containing atom

$\Omega = z\{E_{12} - (E_{11} + E_{22})/2\} = \Delta H_{\text{mixing}}/X_1X_2$: regular solution parameter

z : total number of nearest neighbors

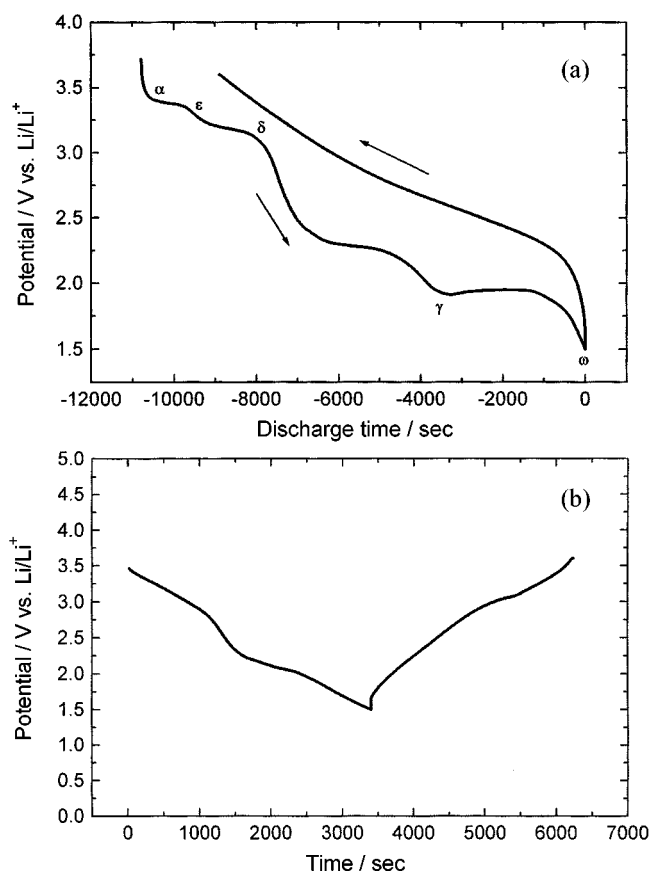


Fig. 5. Potential profiles of the (a) crystalline pure V₂O₅ and (b) Cu_{0.5}V₂O₅ thin film cathode in the cycle.

σ : surface energy, erg/cm²

Thus, surface compositions are a function of surface energy, and alloy profiles in a thin film layer could be estimated theoretically. If we assume σ_1 is a surface energy of copper oxide, copper oxide diffuses from film surface to substrate for its high surface energy than vanadium oxide.

Fig. 5 shows the time vs. potential profile in the range of 1.5–3.6 V (vs. Li/Li⁺) of (a) pure V₂O₅ and (b) Cu_{0.5}V₂O₅ thin film in a half-cell system. Fig. 5(a) shows the typical crystalline V₂O₅ discharge potential profile, which had various phase transformations (α -, ϵ -, δ -, γ -, ω -) as shown in Fig. 3(a). However, Cu-doped V₂O₅ thin film was different from amorphous vanadium oxide cathode which was explained in earlier report [Jeon et al., 2000; Lim et al., 2000], while the S-shaped broad potential drop could be shown continuously for general V₂O₅ cathode materials. That is, first slow potential decrease appears until 2.7 V (vs. Li/Li⁺) and then rapid potential drop is detected in the Cu-doped vanadium oxide case. Also, another slow slope appears lower than 2.1 V (vs. Li/Li⁺). The shape of the curve is similar to the spinel type lithium manganese oxide cathode. Also, the potential profile decrease was less than the typical V₂O₅ cathode material. The exact mechanism is not known clearly, but it is supposed that this potential profile could be due to the copper oxidation states, i.e., from Cu²⁺ to Cu⁺ and from Cu⁺ to metallic Cu as reported by Taketa et al. [1991] and Andrukaitis [1997].

Fig. 6 shows the cycling behavior of the Cu_{0.5}V₂O₅/Lipon/Li type full cell in the range of 1.5–3.6 V, and it was compared to a typical V₂O₅/Lipon/Li from our previous work [Jeon et al., 2000]. The ionic conductivity of Lipon solid electrolyte was measured by blocking electrodes and its value was 1.02×10^{-6} S/cm at 25 °C with composition of Li_{2.94}PO_{3.37}N_{0.75}. It can be shown that the Cu-doped vanadium oxide type cell is more stable than that of original V₂O₅ system beyond 500 cycles [Coustier et al., 1999; Miyazaki et al., 1999; McGraw et al., 1999]. Both cells showed an initial discharge capacity near 80 $\mu\text{Ah}/\text{cm}^2\text{-}\mu\text{m}$ and a slow capacity decay, while the Cu_{0.5}V₂O₅ system was stabilized after 150 cycles. Furthermore, at current density of 50 $\mu\text{A}/\text{cm}^2$ to Cu_{0.5}V₂O₅ system was higher than the pure V₂O₅ system of 20 $\mu\text{A}/\text{cm}^2$.

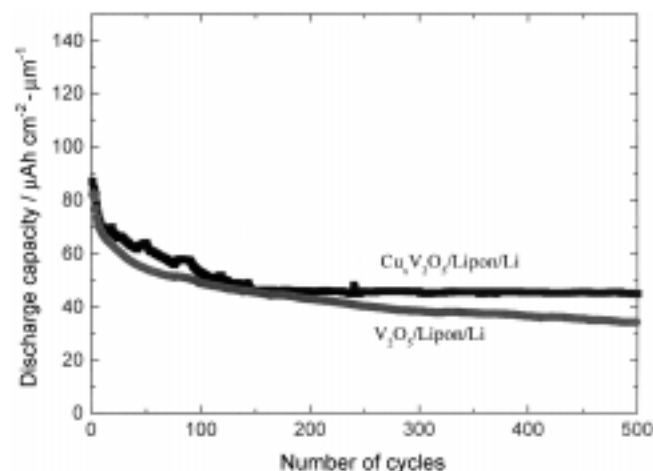


Fig. 6. Cycling behavior of the Cu_{0.5}V₂O₅/Lipon/Li and V₂O₅/Lipon/Li type full cell in the range of 1.5–3.6 V.

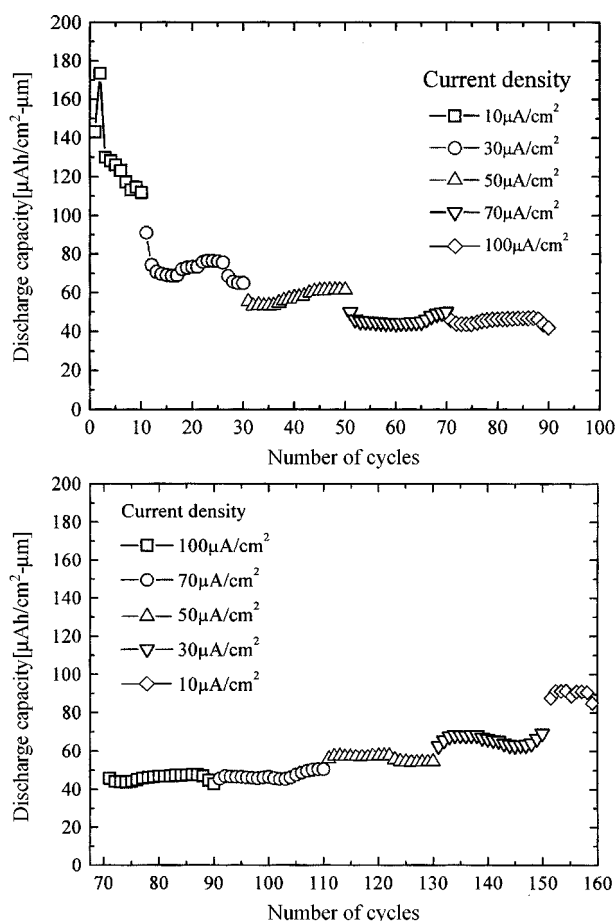


Fig. 7. Rate capability of the $Cu_xV_2O_5$ thin film cathode in a half-cell system.

In the evaluation of battery performance, a rate capability is known as an important factor. It was performed in half-cell system of $Cu_xV_2O_5/1\text{ M LiPF}_6$ in EC : DMC(1 : 1)/Li and the results are shown in Fig. 7. At high current density, above $50\text{ }\mu\text{A}/\text{cm}^2$, it shows stable cyclability and good capacity recovery. From these results, we proved that the $Cu_xV_2O_5$ thin film cathode has high reversible Li^+ intercalation/deintercalation capability.

CONCLUSIONS

Cu-doped vanadium oxide thin film cathode was fabricated by DC reactive magnetron co-sputtering and compared to pure V_2O_5 thin film. It showed an amorphous structure and remarkably different voltage profiles compared to typical V_2O_5 thin film, which showed a slow voltage decay until 2.7 V vs. Li/Li^+ . It was possible to increase film thickness above 1 micrometer with copper doping, resulting in increase of total capacity, while it was hard to grow V_2O_5 thin film thicker than 4,000 Å, because of target poisoning effect during reactive sputtering. The copper content, which was increased in the interface with the substrate, was explained by thermodynamical model. Cycling behavior of the $Cu_xV_2O_5$ based cell system was stabilized after 150 cycles of $50\text{ }\mu\text{Ah}/\text{cm}^2\cdot\mu\text{m}$ and this value is higher than the lithium cobalt oxide or lithium manganese oxide cathode materials. It could offer a possible alternative microbattery system

than typical V_2O_5 cathode material.

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