In Situ Conductivity Measurements during Lithium Intercalation/Deintercalation on V_2O_5 Thin Film by Using Interdigitated Microarray Electrodes

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The conductivity change of a vacuum deposited V_2O_5 thin film during lithium intercalation/deintercalation was investigated using an interdigitated microarray electrode. The conductivity-potential profile showed two peaks (ca. 1.7×10^{-3} S cm^{-1}) at 3.23 V and 3.41 V vs. Li/Li$^+$, corresponding to the peaks in the cyclic voltammogram for Li intercalation/deintercalation. The conductivity decreased below 10^{-5} S cm^{-1} when the potential was scanned to the region more negative than 3.0 V vs. Li/Li$^+$ and an irreversible conductivity change was observed when the potential was scanned back.

Search for cathode materials in high energy density lithium secondary batteries has been vigorously performed by many researchers. Among various materials, V_2O_5 is a potential candidate and has been characterized by electochemical[1-3] and electrospectroscopic[4-6] methods. The conductivity change induced by intercalation/deintercalation is an important characteristics to design high performance batteries. The conductivity of vanadium oxide bronzes ($M_xV_2O_5$, M=aikali metals) has been measured for chemically intercalated materials by *ex situ* measurements[7-9] However, the available data to date are only for a discrete range of x. In this respect, the development of *in situ* measurements is desirable to obtain an intrinsic feature of the Li-intercalated V_2O_5, and a few works has been done for Li intercalation into carbon electrode[10] or WO_3[11] electrode.

In this paper, we report *in situ* conductivity measurements of $Li_xV_2O_5$ film formed on an interdigitated microarray (IDA) electrode. The *in situ* method gives the conductivities in a whole potential region without taking out from the cells[12,13], showing the reliable relationships between conductivity and x in $Li_xV_2O_5$.

Figure 1 shows the IDA electrode and electrochemical apparatus[12,13] for the *in situ* conductivity measurements. The electrical conductivity of the film was determined from the current flowing through the film between two working electrodes (W1, W2).

The IDA electrode was fabricated by photolithography with a sputter-deposited Pt film. A thermal oxidized silicon wafer was used as a substrate. The IDA electrode has two sets of comb-type Pt arrays; each array has 50 electrode elements, 0.1 μm thick, 10 μm wide, and 2.4 mm long, separated by 10 μm from its adjacent elements (Figure 1a). Lead pad of the IDA electrode was insulated with a SiO_2 film. V_2O_5 powder (Kanto Chemical) was vacuum deposited on the IDA electrode at ca. 1×10^{-5} torr to form a V_2O_5 thin film. The thickness of the V_2O_5 film was measured with a surface texture analyzer (DEKTAK 3030ST), and found to be 80~100 nm. The quartz crystal microbalance (Inficon XTM130) measurement indicated that the total mass of the film was ca. 10 μg/cm^2. After the vacuum deposition, the IDA electrode with V_2O_5 film was annealed in air at 500 °C for 1 h. The crystal structure was confirmed by X-ray diffraction. A Li foil was used as a reference and counter electrode. The electrochemical measurements were conducted in propylene carbonate (PC) containing 1 M $LiClO_4$ in a drybox filled with dried Ar.

The potentials of W1 and W2 were controlled by means of a bipotentiostat with a constant bias voltage, 20 mV (Figure 1b). The electrical conductivities of the film were calculated from the ohmic currents flowing through the film bridging over W1 and W2 under dynamic conditions. Steady state conductivity measurements were also carried out. After a fixed amount of Li intercalation/deintercalation was performed at a constant current, the IDA electrode was disconnected from a current source and left until the open circuit voltage reached a steady state. Then, a constant voltage (100 mV) was applied to W1 and W2 to measure the conductivity of the film using a Source Measure Unit (Keythley 236). All the measuremens were carried out at 25°C.

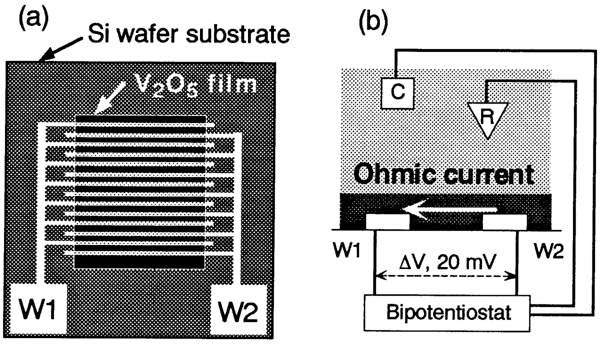

Figure 1. (a) Schematic representation of the IDA for *in situ* conductivity measurements. Electrode width, 10 μm; length, 2.4 mm, 50 elements. (b) Configuration of electrochemical apparatus for *in situ* conductivity measurements. ΔV, potential difference between arrays; W1 and W2, working electrodes (Pt array electrode) ; R, reference electrode (Li); C, counter electrode (Li).

Figure 2 shows an *in situ* potential-conductivity profile (solid line) and a cyclic voltammogram (CV, dashed line) of V_2O_5 film at the IDA electrode. The potentials of W1 and W2 were swept simultaneously with a constant bias voltage, 20 mV. The currents are composed of both the faradaic current for Li intercalation / deintercalation and the ohmic current induced by the bias voltage. If we assume that the magnitudes of the faradaic currents at both arrays are equal, the total currents observed at W1 (i_{W1}) and W2 (i_{W2}) are expressed by,

$$i_{W1} = i_F - i_\Omega, \qquad i_{W2} = i_F + i_\Omega \qquad (1, 2)$$

where i_F is the faradaic current and i_Ω is the ohmic current. The ohmic current can be obtained by,

$$i_\Omega = (i_{W1} - i_{W2})/2 \qquad (3)$$

Conductivities were estimated from the following equation;

$$\sigma = i_\Omega w / 2ldV \qquad (\mathrm{S\ cm^{-1}}) \qquad (4)$$

where w is the gap width of arrays (10 μm), l is the total length of electrode (100 mm), d is the thickness of V_2O_5 film and V is the bias voltage (20 mV).

The conductivity has two peaks (ca. 1.7×10^{-3} S cm^{-1}) at 3.22 V and 3.41 V vs. Li/Li$^+$. These peak potentials coincide with those observed in the CV. Since the crystal structure is ε phase in the potential region between two peaks,[6] it is supposed that ε phase

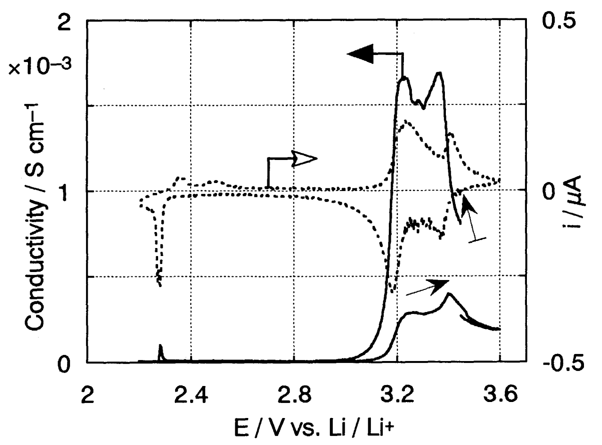

Figure 2. Potential-conductivity profile (solid line) and cyclic voltammogram (dashed line) of V_2O_5 thin film at the IDA in 1 M $LiClO_4$ / PC. Scan rate; 0.1 mV /sec. Bias voltage, 20 mV. Film thickness, 80 nm.

causes the high conductivity. The conductivity-potential profile was reversible when the potential was scanned between 3.0 V and 3.6 V; however, the conductivity decreased steeply as the potential went to negative direction. The conductivities observed at the potentials more negative than 3.0 V were below 10^{-5} S cm^{-1}. When potential was switched back at 2.2 V, the conductivity-potential profile observed on the reversed scan was quite low compared with that on the forward scan. The result suggests that the crystal structure of $Li_xV_2O_5$ changes irreversibly[6] when Li is intercalated in the potentials more negative than 3.0 V. The initial conductivity of V_2O_5 without Li intercalation was ca. 8×10^{-4} S cm^{-1} which was at the same level as the data obtained by Nabavi et. al.[7]

In order to confirm the data obtained by the *in situ* measurement under the potential dynamic condition, the steady-state measurements were also carried out. The measurements provide the steady-state conductivity without faradaic process. Figure 3 shows a potential-steady state conductivity profile and potential-x in $Li_xV_2O_5$. Both profiles show reasonable reversiblity during Li intercalation/ deintercalation, which agrees with the feature observed *in situ* measurements when the potential was scanned between 3.0 V and 3.6 V.

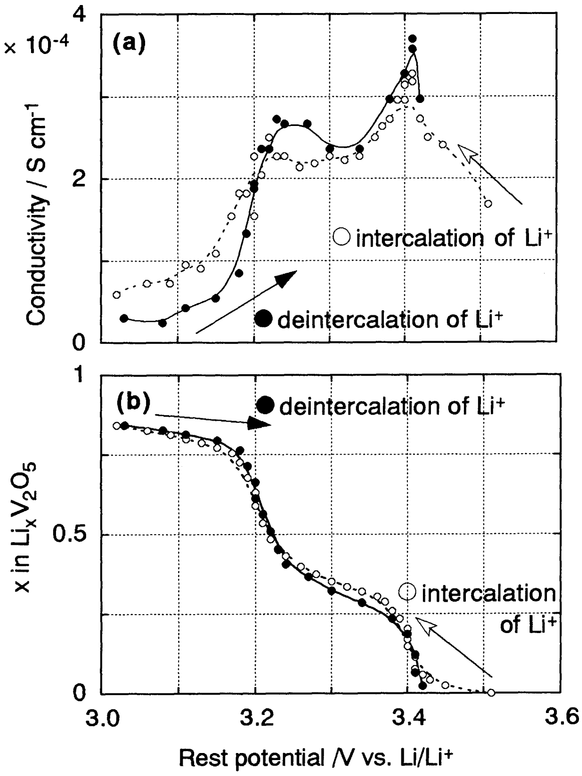

Figure 3. The variation of conductivity (a) and x value (b) of $Li_xV_2O_5$ thin film at IDA as a function of rest potential. The rest potential was recorded after Li intercalation / deintercalation at a constant currrent (0.1 μA). Bias voltage, 100 mV. The mass of the V_2O_5 film, 3.88 ×10^{-9} mol (0.705 μg). Film thickness, 110 nm.

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