Fabrication of Thin Film Electrodes of Li-Ni-Mn-O Using PVP Sol-Gel Coating Method

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Introduction

Lithium nickel manganese oxides are promising materials as cathode of rechargeable lithium batteries. Many research groups reported electrochemical properties and structural characteristics of these materials. $LiNi_{0.5}Mn_{1.5}O_4$ has been investigated as a 5 V class cathode material of Li-ion battery. $LiNi_{0.5}Mn_{0.5}O_2$ has a layered structure, and large discharge capacity and long cycle life of this material have been reported[1].

In our previous paper[2], we reported that thin film electrodes of $LiCoO_2$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$ for rechargeable lithium batteries can be prepared by using a sol-gel coating method with poly(vinylpyrrolidone) (PVP). In the present study, thin films of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{0.5}O_2$ were fabricated and their crystallographic structures and electrochemical properties were evaluated.

Experimental

A molar ratio of each component in the Li-Ni-Mn-O sol for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{0.5}O_2$ was shown in Table 1. The sol of $LiNi_{0.5}Mn_{0.5}O_2$ was prepared from acetate or nitrate. Each sol was coated on Au substrate by spin coater above 3000 rpm. During this process, the sol film was converted to the gel. The prepared gel films of $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{0.5}O_2$ were heated at 800 °C for 60 min, and 600-900 °C for 10-120 min, respectively. Their surface morphology was observed with a scanning electron microscope (SEM). Crystallographic structures were characterized by X-ray diffraction (XRD) and Raman spectroscopy. The cyclic voltammetry (CV) was employed to examine the electrochemical activity of samples.

Results and Discussion

Figure 1 shows the cyclic voltammograms of the prepared $LiNi_{0.5}Mn_{1.5}O_4$ thin film electrode. As shown in Fig. 1, reversible peaks are observed at about 4.0V and 4.7V, those are intrinsic electrochemical properties of the material. The small peak at 4.0 V indicates that Mn^{3+} remains in the structure. Figure 2(a) shows Raman spectrum of $LiNi_{0.5}Mn_{1.5}O_4$ sample, which is consistent with the results reported in the literature[3]. Figure 2(b) shows the Raman spectrum of $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrode, which is different from that of $LiNi_{0.5}Mn_{1.5}O_4$ thin film. The two peaks at 500cm^{-1} and 590cm^{-1} were recognized. The assignments of Raman peaks were not clear at present. Further investigations including XRD and electrochemical measurements are underway. The detailed electrochemical properties of $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrode will be also reported.

References

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[3] K. Dokko, M. Mohamedi, N. Anzue, T. Itoh, and I. Uchida, *J. Mater. Chem.*, **12**, 3688-3693 (2002).

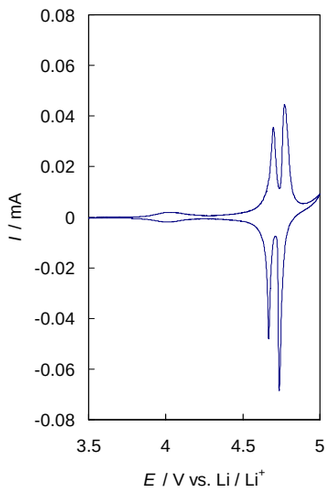

Figure 1. CV of $LiNi_{0.5}Mn_{1.5}O_4$ electrode prepared at 800 °C for 1hour in electrolyte at 10 mV min^{-1} (1.0 mol dm^{-3} $LiPF_6$ (EC+EMC / 1:1(volume ratio))).

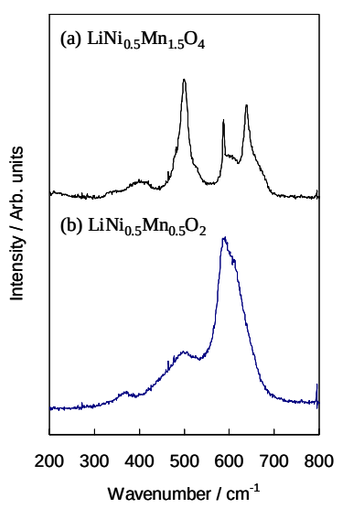

Figure 2. Raman spectra of (a) $LiNi_{0.5}Mn_{1.5}O_4$ and (b) $LiNi_{0.5}Mn_{0.5}O_2$ thin film electrodes prepared by using a PVP sol-gel method.

Table 1. A molar ratio of each component in Li-Ni-Mn-O sol for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiNi_{0.5}Mn_{0.5}O_2$.

acetate	CH_3COOLi	$Ni(CH_3COO)_2{\cdot}4H_2O$	$Mn(CH_3COO)_2{\cdot}4H_2O$	PVP	CH_3COOH	H_2O	*i*-C_3H_7OH
$LiNi_{0.5}Mn_{1.5}O_4$	1	0.55	1.5	1.5	45	47.5	40
$LiNi_{0.5}Mn_{0.5}O_2$	1.1	0.55	0.5	1.5	45	45	40
nitrate	$LiNO_3$	$Ni(NO_3)_2{\cdot}6H_2O$	$Mn(NO_3)_2{\cdot}6H_2O$	PVP	CH_3COOH	H_2O	*i*-C_3H_7OH
$LiNi_{0.5}Mn_{0.5}O_2$	1.1	0.5	0.5	1.5	15	20	40