## Preparation of LiMn₂O₄ Thin-Film Electrode with High Electrochemical Performance by the Oxygen Plasma-Assisted Sol-Gel Method

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### Introduction

Solution-based methods give spinel-type lithium manganese oxide ($LiMn_2O_4$) with a fine particle size, a narrow size distribution and uniform composition, which leads to high electrochemical performance. In these solution-based methods, the precursors usually contain organic materials to maintain the Li-Mn-O framework. Carbon atoms must be eliminated from the precursors for relatively high-temperature firing. High-temperature firing promotes the growth of $LiMn_2O_4$ particles. The heat of combustion generated by the firing of carbon atoms also leads to the growth of $LiMn_2O_4$ particles. Large particles of $LiMn_2O_4$ impair the rate performance of lithium-ion batteries. Therefore, carbon atoms must be eliminated to obtain fine-particle $LiMn_2O_4$ by solution-based methods. The elimination of carbon atoms from precursors should make lower-temperature synthesis and suppression of combustion possible. We focused on oxygen plasma treatment to eliminate carbon atoms from precursors. In this study, we report a new method for preparing a $LiMn_2O_4$ thin-film electrode with high electrochemical performance by the oxygen plasma-assisted sol-gel method at a lower temperature.

### Experimental

Li-Mn-O precursor was prepared by the sol-gel method using PVP (poly(vinylpyrrolidone) as reported by Kanamura et al. [1], since the sol or gel obtained by this method is very stable. $CH_3COOLi$ was selected as a lithium source and $Mn(CH_3COO)_2 \cdot 4H_2O$ as a manganese source. The solvents were ethanol, water and acetic acid. Li-Mn-O sol was spin-coated onto a Pt sheet and dried at 393 K to obtain a precursor thin film. The precursor thin film was exposed with oxygen plasma for 1 h. The detail of the plasma-treatment chamber has been described previously [2]. The treated precursor thin film was fired at 723 K for 2 h in air, and $LiMn_2O_4$ thin film was obtained. Hereafter, the $LiMn_2O_4$ thin film obtained by the above process is referred to as PA-LMO-723. For comparison, untreated precursor thin film was also fired at 723 K, and the resultant thin film is referred to as LMO-723. XRD measurement and Raman spectroscopy were used to characterize the resultant thin films. Atomic force microscopy (AFM) observation was carried out to evaluate the particle size of the resultant thin films. Electrochemical properties were studied by cyclic voltammetry (CV) using a three-electrode cell. A $LiMn_2O_4$ thin-film electrode was used as a working electrode. Lithium metal was used as both counter and reference electrodes. Electrolytes consisting of PC containing 1 mol dm⁻³ $LiClO_4$ were used. All experiments were conducted under an Ar atmosphere. Unless otherwise stated, the potential is referenced to against $Li/Li^+$.

### Results and discussion

In XRD pattern of PA-LMO-723, weak peaks were observed at about $2\theta = 19°$ and $36.5°$, corresponding to the (111) and (311) planes, indicating the formation of spinel-$LiMn_2O_4$. Micro-Raman spectroscopy was used to characterize the surface crystallinity of PA-LMO-723. In the Raman spectrum, broad peaks appeared at around 640 cm⁻¹. The peak at around 640 cm⁻¹ can be divided into two peaks at around 630 cm⁻¹ and 650 cm⁻¹. The peak at around 630 cm⁻¹ is assigned to the symmetric $A_{1g}$ mode of the $LiMn_2O_4$ spinel phase. The peak at around 650 cm⁻¹ might show the existence of $Mn_2O_3$. There is no clear difference between PA-LMO-723 and LMO-723 in their XRD patterns and Raman spectra. These results suggest that oxygen plasma-assist did not influence the crystallinity of the surface or that of the interior bulk of $LiMn_2O_4$. AFM observation was conducted to clarify the influence of oxygen plasma-assist on the particle size of PA-LMO-723. **Figure 1** shows AFM images of PA-LMO-723. The particle sizes of PA-LMO-723 are much smaller and the particles were uniformly dispersed. This result suggests that oxygen plasma-assist suppressed the growth of $LiMn_2O_4$ particles.

The above results suggest that particle growth was suppressed. Next, the influence of oxygen plasma-assist on the lithium ion extraction/insertion behavior of the thin-film electrode was examined by cyclic voltammetry. As shown in **Fig. 2**, LMO-723 shows two pairs of redox peaks at around 4.00 V and 4.15 V. The two oxidative peaks were not clearly separated. In contrast, two oxidative peaks (4.00 V and 4.15 V) were clearly separated for PA-LMO-723. This is due to the small diffusion path within $LiMn_2O_4$. The electrochemical properties of the resultant $LiMn_2O_4$ thin-film electrode prepared at a lower temperature were greatly improved. The oxygen plasma-assisted sol-gel method should be useful for obtaining fine particles of active materials in lithium-ion batteries. The detail will be presented in the poster.
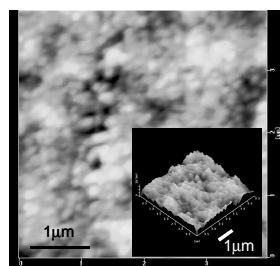


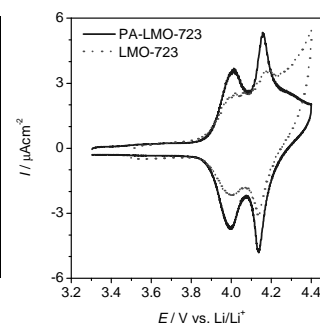**Fig. 1.** AFM images of $LiMn_2O_4$ thin films with oxygen plasma-assist (PA-LMO-723).

**Fig. 2.** CVs (1st cycle) of $LiMn_2O_4$ thin-film electrodes (PA-LMO-723 and LMO-723) in 1 mol dm⁻³ $LiClO_4$ / PC. Scanning rate is 0.1 mV/s.

### References
[1] Y. H. Rho, K. Kanamura, and T. Umegaki, *J. Electrochem. Soc.*, **150**, A107 (2003).
[2] T. Fukutsuka, S. Hasegawa, T. Katayama, Y. Matsuo, Y. Sugie, T. Abe and Z. Ogumi, *Electrochemistry*, **71**, 1111 (2003).