A time-resolved quadrupole mass spectrometric study on 355 nm laser ablated species ejected from LiMn$_2$O$_4$

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Abstract    Mass, velocity and angle distributions of the ablated species generated from 355 nm pulsed laser ablation of a LiMn$_2$O$_4$ target were investigated with an angle- and time-resolved mass spectrometric technique. Both neutral and ionic species of Li, O, LiO, LiO$_2$, Mn, Li$_2$, Li$_4$, Li$_6$, LiMn, MnO and MnO$_2$ were observed at the laser fluence of 0.8 J cm$^{-2}$. The yield and variety of the ablated species increase with increasing the laser fluence. The time-of-flight spectra of ablated species can be fitted by a Maxwell-Boltzmann distribution with a center-of-mass velocity. There exist laser fluence thresholds for the ablated LiMn, Li$_2$O and LiO$_2$ species, and the fluence threshold of ionic species is higher than that of neutral species. The angular distributions of the ionic and neutral ablated species can be simulated by a cos$^n\theta$ or a bicosine function $\alpha \cos \theta + (1-\alpha)\cos^2 \theta$. In addition, the ablation mechanism of LiMn$_2$O$_4$ by a 355 nm pulsed laser is discussed.

Keywords: LiMn$_2$O$_4$, laser ablation, TOF, angular distribution.

Recently, all-solid-state thin film rechargeable lithium batteries have been investigated extensively because of their high energy density, superior charge-discharge property and safety$^{[1]}$. The study of novel cathode materials has been an important subject. In comparison with LiNiO$_2$ and LiCoO$_2$, LiMn$_2$O$_4$ is the most promising candidate due to its high theoretical energy density, low cost and less toxicity$^{[2]}$. LiMn$_2$O$_4$ thin films have been prepared by various methods including RF sputtering, electron beam deposition and pulsed laser deposition (PLD)$^{[3]}$. The capability of depositing high quality films with nearly the original stoichiometry of a bulk target and high deposition rate make PLD technique an attractive method for the fabrication of thin films. LiMn$_2$O$_4$ thin films have been prepared by PLD$^{[4,5]}$, however, the previous studies usually focused on their fabrication process and electrochemical properties and rarely on the physico-chemical process of the laser ablation of LiMn$_2$O$_4$. In our laboratory, we have successfully prepared thin film electrodes for Li-ion batteries and electrochromic devices, high dielectric materials and photoluminescence films using PLD method. In order to extend our understanding of the thin film formation and the nature of the laser ablation process, we have carried out the identification of neutral and ionic ablated species as well as the determination of their kinetic energy and spatial distributions$^{[6-10]}$, since the measurements of the angular distributions of the ablated species can provide important information on the expansion dynamics of the ablated plume as well as the chemical composition and thickness uniformity of the deposited film. In this paper, we measure
the mass, kinetic energy and spatial distributions of ablated species ejected from a LiMn$_2$O$_4$ target using angle- and time-resolved quadrupole mass spectrometric method. The ablation mechanism of LiMn$_2$O$_4$ by a 355 nm pulsed laser is also discussed.

1 Experimental

The experimental apparatus used for angle- and time-resolved mass spectrometry has been described previously\[^{11}\]. Briefly, a 355 nm laser beam was provided by the third harmonic of a Q-switched Nd:YAG laser (Spectra Physics, GCR-190) with a pulse duration of 6 ns and a repetition rate of 10 Hz. The laser fluence was measured by a power meter with a pyroelectric detector. The laser beam was focused on a target surface with an incidence angle of 45°. The target was mounted on a rotatable target holder at the center of a reaction chamber. The LiMn$_2$O$_4$ pellet as a target was obtained by uniaxially compressing pure LiMn$_2$O$_4$ powder and subsequently being calcined at 1073 K for 5 h. The ablated species were detected by a quadrupole mass spectrometer (QMS, ULVAC MSQ-400), which can be moved around the reaction center of the ablation chamber in the range of 0—90° to detect the angular distributions of the ablated species. The time-of-flight spectra (TOF) of the ablated species were measured with a 20 MHz transient recorder and triggered synchronously by the laser pulse. The flight distance of ablated species was 18 cm. Nascent ionic species were detected with the ionizer of QMS switched off and both ionic and neutral species were recorded when the ionizer was switched on. Subtracting the signal of nascent ionic species from the total signal with the ionizer switched on gives the signal of neutral species. Taking into consideration of the drift time of the ablated species in the quadruple mass spectrometer, the measured TOF spectra should be calibrated for the drift time of ions in the QMS with $4.15M^{1/2}$\[^{12}\], where $M$ is the mass of the ablated species under our experimental conditions. The relative yields of the ablated species were obtained by integrating the corresponding TOF spectra.

2 Results and discussion

2.1 Mass distributions and TOF spectra of the ablated species

Fig. 1 presents the mass distributions of the nascent ionic and neutral species generated from the laser ablation of the LiMn$_2$O$_4$ target, in which the signal of O$_2$ is not shown since its relative intensity is too strong. It can be seen that the observed ablated species are: both ionic and neutral Li ($m/e$ = 7), O ($m/e$ = 16), LiO ($m/e$ = 23), LiO$_2$ ($m/e$ = 39), Mn ($m/e$ = 55), and neutral Li$_4$ ($m/e$ = 28), Li$_6$ ($m/e$ = 42), LiMn ($m/e$ = 62), MnO ($m/e$ = 71), MnO$_2$ ($m/e$ = 87) at a laser fluence of 0.8 J · cm$^{-2}$. At a laser fluence of 2.0 J · cm$^{-2}$, however, besides those detecting species, other unusual ionic and neutral clusters, such as LiMnO($m/e$ = 78) and Mn$_2$($m/e$ = 110) can be observed.

As shown in fig. 1, the intensities of the neutral species are higher than those of the ionic species. The very high ablation yield of oxygen in ablated species usually results in the deficiency of oxygen in the deposited thin film. So, the laser reactive ablation in an O$_2$ ambient is generally