

# Reaction Mechanism of $\text{Li}_2\text{MnO}_3$ Epitaxial Film Electrodes in All-Solid-State Thin Film Batteries

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Lithium-rich layered rocksalt type  $\text{Li}_2\text{MnO}_3$  is an attractive cathode material for lithium batteries due to its high capacity (over 250 mAh  $\text{g}^{-1}$ ) after an activation process during the first cycling [1]. However, subsequent cycles at the cathode/liquid electrolyte interface induce structural deterioration, leading to severe capacity fading. Herein we report the charge-discharge properties of 40 nm-thick epitaxial  $\text{Li}_2\text{MnO}_3$  films in all-solid-state batteries, which have the potential to overcome the poor stability.

Pulsed laser deposition synthesized electrode films with a 001 orientation on  $\text{Al}_2\text{O}_3(0001)$  substrates. Amorphous  $\text{Li}_3\text{PO}_4$  and lithium metal were used as the solid electrolyte and the negative electrode, respectively. The electrochemical reactions at the interfaces were analyzed based on the interfacial structures determined by *in situ* X-ray diffraction (XRD) measurements.

Unlike a battery with a liquid electrolyte, which shows severe capacity fading and structural deterioration, the all-solid-state battery does not exhibit significant capacity fading and has a high coulombic efficiency during 100 cycles. Table 1 shows the XRD intensity ratio of  $I_{020}/I_{001}$  and  $I_{-202}/I_{001}$  or  $I_{131}/I_{001}$  for the liquid and solid systems. For both systems,  $I_{020}/I_{001}$  becomes zero after the activation process. Since the 020 diffraction peak arises from the superlattice structure by a honeycomb-type ordered arrangement of Li and Mn atoms in the transition metal (TM) layer, the atomic arrangements in the TM layer transform into a disordered state in both systems. The value of  $I_{-202(131)}/I_{001}$  indicates the amount of Mn migrating to the Li layer from the TM layer. For the solid system, an obvious change in the cell construction to the tenth cycle is not observed, indicating that disordering of Li and Mn (or vacancy) occurs only in the TM layer. In addition, *ex situ* XPS measurements detect the interfacial layer after the first cycle. The changes in the crystal structure and the interfacial layer after activation in the all-solid-state battery may contribute to its high capacity and high cycle stability after the activation process.

Table 1 XRD intensity ratio of  $I_{020}/I_{001}$  and  $I_{-202(131)}/I_{001}$  at a liquid and solid system.

States	Liquid battery		All-solid-state battery	
	$I_{020}/I_{001}$	$I_{-202}/I_{001}$	$I_{020}/I_{001}$	$I_{131}/I_{001}$
OCV	~0	1.0	0.10	1.0
1st charge	0	0.81	0.12	1.1
1st discharge	0	0.48	0.09	1.0
2nd discharge	0	0.27	0.02	1.0
10th discharge	0	0.16	0	1.1

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**Reference** [1] M. Sathiyaraj *et al.*, *Nat. Mater.*, 12, 827-835 (2013).