

Perpetual Battery Cycling for Epitaxial LiMn₂O₄ Thin Film Cathodes

Theodoor A. Hendriks^a, Daniel M. Cunha^a, Deepak P. Singh^a, Mark Huijben^a

^a University of Twente, Faculty of Science and Technology, 7522NH, Enschede, The Netherlands

E-mail: t.a.hendriks@utwente.nl

Detailed understanding of the electrochemical behavior of specific crystal facets in battery devices can only be obtained when a single type of crystal orientation interfacing the electrolyte can be synthesized. This can be achieved by epitaxial thin film technology. Most studies on LiMn₂O₄ thin films have investigated polycrystalline samples, while only limited research has been performed on single crystalline thin films [1-5]. Characterization of epitaxial thin films has previously been focused on the structural properties, only few reports have shown electrochemical properties by clear redox peaks and discharge capacities around 125 mA·h·g⁻¹ with clear plateau regions in the (dis-)charge curves [3-5]. A study by Hirayama et al. concluded from surface X-ray diffraction measurements that a solid-electrolyte interface (SEI) was present on both (111) and (110) surfaces, although the (110) surface was less stable and indicated a higher Mn dissolution [2]. Unfortunately, the actual electrochemical performance was only studied for LiMn₂O₄ thin films grown on (111)-oriented SrTiO₃ substrates [3,4].

Here, we will show that by structural engineering of stable, epitaxial LiMn₂O₄ thin films the electrochemical properties can be controlled and enhanced as compared to polycrystalline samples. By changing the crystal orientation of the single crystalline Nb:SrTiO₃ (0,5wt%) substrate ((100), (110) and (111)) we can control the specific orientation of the LiMn₂O₄ thin film and, therefore, the cathode surface towards the adjacent electrolyte. We demonstrate the realization of epitaxial cathode thin films exhibiting high capacity >90% of theoretical limit, fast (dis)charging rates of 1-20C and excellent cyclability over hundreds of cycles. All three crystal orientations showed similar high electrochemical performance without any significant capacity fading, indicating the realization of perpetual behavior ideal for battery devices.

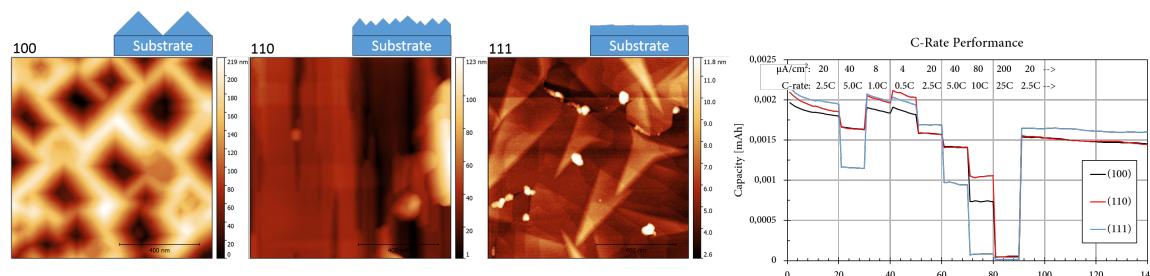


Figure (Left) Three panels showing the surface topographies of LiMn₂O₄ films with different crystal orientations (scale bar is 400 nm) and (right) panel showing the C-rate performance.

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