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Origin of electrochemical activity in nano-Li₂MnO₃; stabilization via a 'point defect scaffold'

Thi X. T. Sayle,^{ab} Francesco Caddeo,^a Nkwe O. Monama,^{bc} Kenneth M. Kgatwane,^b Phuti E. Ngoepe^b and Dean C. Sayle^{*a}

* Corresponding authors

^a School of Physical Sciences, University of Kent, Canterbury, CT2 7NZ, UK

E-mail: d.c.sayle@kent.ac.uk

^b Materials Modelling Centre, University of Limpopo, Private Bag x1106, Sovenga, South Africa

^c Centre for High Performance Computing, CSIR, 15 Lower Hope Rd, Cape Town 7700, South Africa

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Abstract

Molecular dynamics (MD) simulations of the charging of Li₂MnO₃ reveal that the reason nanocrystalline-Li₂MnO₃ is electrochemically active, in contrast to the parent bulk-Li₂MnO₃, is because in the nanomaterial the tunnels, in which the Li ions reside, are held apart by Mn ions, which act as a pseudo 'point defect scaffold'. The Li ions are then able to diffuse, via a vacancy driven mechanism, throughout the nanomaterial in all spatial dimensions while the 'Mn defect scaffold' maintains the structural integrity of the layered structure during charging. Our findings reveal that oxides, which comprise cation disorder, can be potential candidates for electrodes in rechargeable Li-ion batteries. Moreover, we propose that the concept of a 'point defect scaffold' might manifest as a more general phenomenon, which can be exploited to engineer, for example, two or three-dimensional strain within a host material and can be fine-tuned to optimize properties, such as ionic conductivity.