

Insight into Fast Li diffusion in Li-excess spinel lithium manganese oxide

Weiji Xiao ^a, Chao Xin ^b, Sibai Li ^a, Jianshu Jie ^a, Yue Gu ^a, Jiaxin Zheng ^a and Feng Pan ^a

^a *School of Advanced Materials, Peking University, Shenzhen Graduate School, Shenzhen, 518055, China*

^b *School of Science, Changchun University of Science and Technology, Changchun 130000, China*

E-mail: panfeng@pkusz.edu.cn

Li-excess cathode materials are expected to have great potential for applications in lithium-ion batteries for their high energy density. Besides the extensive studies on the anionic redox activity in them, their Li-ion diffusion properties have also attracted much interest. Using *ab initio* calculations, here we systematically explored Li diffusion properties in both stoichiometric and Li-excess phase of spinel lithium manganese oxide (LMO). Our results show that there is a kind of structure unit (six Mn forming a cation ring for Li-ion passing through during migration) to play as “gate sites”, and the Li-excess configuration can introduce two kinds of fast Li-ion migration channels to enhance the Li-ion diffusivity. The first kind of fast channels result from that the Li⁺ substitution of Mn³⁺ can decrease the Coulomb repulsion interactions between the cations at the gate site and the mobile Li-ion. The second kind of fast channels originate from that the excess Li can induce more gate sites with symmetrical distribution of Mn⁴⁺ surrounding the Li diffusion channel, which is proved to be able to enhance the Li-ion mobility. Interestingly, it is also found that in the slow Li diffusion channels for both stoichiometric and Li-excess LMO, a simultaneous polaron hopping process around the gate sites will be coupled to the Li migration process, which accounts for the high energy barriers of Li-ion diffusion.