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

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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.