Investigation of the Mechanisms of Polaron Conduction in Cathode Materials of Na and K-Ion Batteries.

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Due to increasing demand in stationary and portable energy storage an extensive research of new electrode materials for metal-ion batteries is performed nowadays. In contrast to Li-ion, sodium ion and potassium ion batteries are cheaper and allows to mitigate the risks associated with lithium production concentrated in a few countries, while Na is one of the most abundant elements on Earth. However, sodium-based materials are suffering from poor electronic conductivity such as in the case of hexacyanoferrate (HCF) based cathode, e.g. $Na_2Fe_2(CN)_6$ [1]. The electronic transport in HCF and other insulating cathode materials proceeds by the polaron hopping mechanism calling for its thorough investigation as it has a strong impact on a battery rate performance.

According to experimental results the rate performance of $KTiOPO_4$-type based (KTP) cathode materials ($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) is several orders of magnitude higher than that of hexacyanoferrate based (HCF) materials ($Na_2Fe_2(CN)_6$) [2, 3]. However, it remains unclear what are the physical reasons for the observed differences between these two classes of materials. There is a hypothesis that it originates from the different transport of small polaronas. Unfortunately, little is known about the small polaron behavior in either of the two classes of materials. Therefore, in this study we perform a computational study of small polaron transport using Density Functional Theory (DFT) by calculating polaron migration barriers and polaron formation energies.

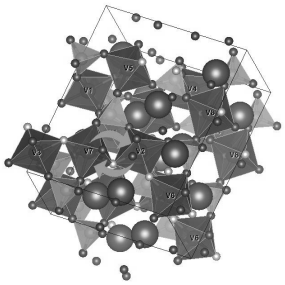

Figure 1. KTP-type structure and directions of investigated polaron hoppings.

All materials are modeled using generalized gradient approximation (GGA) with Hubbard correction and standard PAW PBE potentials as implemented in VASP software. To form an electron (hole) small polaron we add (remove) one electron and slightly distort a required octahedron by adjusting M-O, F distances. To calculate migration path we use a linear interpolation scheme $q(x) = xq_A + (1 - x)q_B$, where $0 < x < 1$, q_A — structure with polaron on initial site, q_B - with polaron on final site. We investigate migration barriers of hole polarons for intercalated structures ($NaVPO_4F$, $KVPO_4F$, $KTiPO_4F$) and electron polarons for deintercaleted structures (VPO4F, TiPO4F).

By comparing several compounds with the same crystal structure but different chemical composition we rationalized the impact of alkali and transition metal elements on the formation and migration energies of polarons. For non-equivalent TM sites the polaron formation energies can differ by up to 0.25 eV causing an additional increase of migration barriers. The polaron localization is more preferable for more symmetric octahedra, while fluorine displacement has strong impact on polaron formation. The calculated migration barriers suggest that the electronic conductivity should decrease in the following order: $KVPO_4F$ > $NaVPO_4F$ > VPO_4F > $KTiPO_4F$ > $TiPO_4F$, respectively. The smallest barrier of 0.18 eV was obtained for $KVPO_4F$, which is smaller than that in commercially produced $LiFePO_4$ [4]. The preliminary results confirm the proposed hypothesis that the polaron migration barriers in KTP are smaller than that in HCF materials. This results explains the origin of high performance of KTP materials and provide a rationale for their further optimization.

References

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