Sodium Diffusion Mechanism and (De)Intercalation in NASICON Molybdates NaMR(MoO$_4$)$_3$ ($M =$ Mg, Ni; $R =$ Cr, Fe): Ab Initio Study

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ABSTRACT

Currently, intensive studies are devoted to the search for new electrolyte and electrode materials with fast sodium diffusion, high voltage, and long charging/discharging cycles. NASICON-structured compounds attract scientific attention as perspective cathode materials for sodium-ion batteries due to their good electrochemical properties [1–4]. Besides, the NASICON structure has cavities for intercalation of up to three Na atoms per formula unit, which makes it possible to use these compounds as anode materials. Recently, molybdates with NASICON structure were proposed as perspective materials for sodium-ion batteries [5].

We present the results of first-principles simulation of the electronic structure, sodium diffusion and (de)intercalation mechanism in NaMR(MoO$_4$)$_3$ ($M =$ Mg, Ni; $R =$ Cr, Fe) with NASICON structure. Using the GGA+U approach, we predict semiconductor behaviour with the antiferromagnetic ground state in all studied molybdates. According to our calculations, barriers for Na-hops in these materials depend on the vacancy formation energy at the initial and final position of the hop. Our simulations predict lower barriers of the 3D sodium diffusion for NaMgR(MoO$_4$)$_3$ (0.6 eV), than for NaNiR(MoO$_4$)$_3$ (0.8–0.9 eV). We studied the (de)intercalation process in Na$_x$MR(MoO$_4$)$_3$ and found that sodium extraction should occur at a high voltage (4.6–5.7 V), and intercalation – at a low voltage of 0.7–1.0 V. The operating range of reversible cycling was established using calculations of the voltage profile, as well as changes in cell volume and enthalpy of formation depending on the $x$ values in Na$_x$MR(MoO$_4$)$_3$. Our results demonstrate that molybdates NaMR(MoO$_4$)$_3$ ($M =$ Mg, Ni; $R =$ Cr, Fe) have diffusion and redox properties similar to the known sulphates and phosphates, and can also be promising cathode and anode materials for sodium-ion batteries.

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REFERENCES