

# Surveying Ilmenite Type 4d Transition Metal Oxides for Na Ion Battery Cathodes with High Potential and High Capacity

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We present a comprehensive density functional study screening the full range of ternary hexagonal layered compounds of ilmenite type structure (space group 148,  $R\bar{3}$ ) that consist of Na, O and 4d transition metal (TM) elements in search for candidates with high potential and large capacity for sodium ion battery cathodes.

Computationally, we treated the exchange correlation functional with GGA+ $U$  formalism.  $U$  term was particularly fine-tuned to reproduce the electrochemical potential of Na extraction in  $\text{Na}_x\text{RuO}_3$  compound for which measurements exist [1]. We found that  $U = 2$  eV fulfils this criterion and moreover it produces an electronic structure that resembles the one obtained with higher level HSE03 functional.

As presented in Table 1, our results indicate oxygen's significant participation in the redox reaction in a number of compounds such as  $\text{Na}_1\text{NbO}_3$ ,  $\text{Na}_1\text{RuO}_3$ , etc. The availability of O electrons for redox reaction originates from the local coordination environment. In  $\text{Na}_1\text{TMO}_3$  ilmenite structure, O ions are coordinated by two TM ions and two Na ions. Consequently, O under-coordination elevates some of un-hybridized or *orphaned* O 2p states closer to the Fermi level and thus facilitates continuous O redox over a wide range of Na concentrations. Although this mechanism, to some extent, resembles the pure reversible O redox in 3d transition metal oxides [2], however, due to weaker localization effects of 4d transition metals, some TM–O hybridization always exists. This hybridization together with relatively large O–O separation prevent the detrimental  $\text{O}_2$  evolution in these compounds. Judging from O participation in redox, potential and stability against competing phases [3],  $\text{Na}_1\text{NbO}_3$  compound is identified as an economical and superior Na ion cathode.

Table 1. Na vacancy formation energy, O population near the Fermi level ( $-2 < E < E_{\text{Fermi}}$ ) and the shortest O–O distance for surveyed compounds. Vacancy formation energy is proportional to the cathode potential, O population is indicative of O participation in redox and the shortest O–O distance is a predictive of adverse  $\text{O}_2$  evolution.

System	$\text{Na}_1\text{NbO}_3$	$\text{Na}_1\text{MoO}_3$	$\text{Na}_1\text{TcO}_3$	$\text{Na}_1\text{RuO}_3$	$\text{Na}_1\text{RhO}_3$	$\text{Na}_1\text{PdO}_3$	$\text{Na}_1\text{AgO}_3$
$E^{\text{f}}$ of $V_{\text{Na}}$ (eV)	4.94	2.62	2.90	3.72	3.63	4.08	4.66
O population (e/O)	2.58	0.16	0.38	1.40	1.50	2.10	2.51
O–O (Å)	2.58	2.53	2.49	2.51	2.53	2.59	2.64

## References

- [1] B. M. de Boisse, M. Okubo, A. Yamada *et al.*, Nat. Commun., 7 (2016) 11397.
- [2] D.-H. Seo, *et al.*, Nat. Chem., 8 (2016) 692–697.
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