Na-ion intercalation in mixed-termination $Ti_3C_2T_x$ and V_2CT_x multilayers from first-principles

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The demand for high-performance electrochemical storage devices has risen dramatically in recent times, necessitating the development of novel electrode materials for the next generation of renewable energy devices. Layered two-dimensional (2D) materials, which can intercalate metal atoms between their layers, are potential candidates, particularly those which show promising electroactivity for metals beyond Li, such as Na, K or Mg. In this regard, the family of MXene materials appear favourable. These layered materials are produced from their parent $M_{n+1}AX_n$ phases through a selective chemical etching of the covalently bonded A layer (M is an early transition metal, A is typically aluminium, X is either C or N and $n = 1 - 3$). Due to the etching process, the MXene layers are generally covered by mixed termination groups, predominately -O, -F and -OH. These terminating groups are known to be randomly distributed over the surface with limited experimental control over their stoichiometry [1, 2]. Their exact composition has been shown to have a significant effect on the structural, electronic and electrochemical behaviour of the MXene layers [3]. However, most theoretical investigations of their ability to act as electrodes in Na-based electrochemical devices make a significant simplification; they assume the MXene surface is covered by uniform terminations of -O, -F or -OH groups rather than randomly mixed terminations. Here, we use density functional theory (DFT) calculations to systematically investigate two of the most popular members of the MXene family, namely $Ti_3C_2T_x$ and V_2CT_x, where now T_x represents an experimentally determined termination stoichiometry. I show how the structural and electronic properties of these structures differ from those which assume uniform terminations and compare the results to available experimental data. While the properties of the un-intercalated materials can be, to a large extent, captured by a simple weighted average of the properties of the uniformly terminated structures, the intercalation of Na depends more sensitively on the terminating groups. I show that the redox reaction is initially confined to the terminating groups while the oxidation state of the metal atoms is not increased until a higher Na concentration is achieved. Finally, I discuss the how the particular composition of the terminating groups can tune the open circuit voltage (OCV) of both materials over a range of approximately 0.4eV.

References

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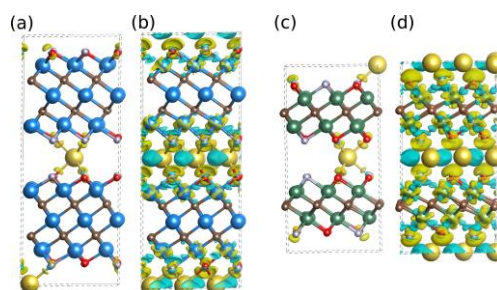
Figures

Figure 1: Charge density difference plots for (a) 0.11 ML, (b) 1 ML Na atom intercalated into a 3 x 3 super-cell of mixed-terminated $Ti_3C_2T_x$ (c) 0.11 ML, (d) 1 ML Na atom intercalated into a 3 x 3 super-cell of V_2CT_x.