Role of surface terminations on the mono- and multi-valent ion capacity of MXenes

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MXenes, a family of layered transition metal carbides and nitrides, have shown great promise for use in emerging electrochemical energy storage devices, including batteries and supercapacitors.

MXene surfaces are terminated by mixed –O, –F and –OH functional groups as a result of the chemical etching production process. These functional groups are known to be randomly distributed over the surfaces, with limited experimental control over their composition. There is considerable debate regarding the contribution of these functional groups to the properties of the underlying MXene material. For instance, their measured Li or Na capacity is far lower than that predicted by theoretical simulations, which generally assume uniformly terminated surfaces. The extent to which this structural simplification contributes to such discrepancies is unknown.

We address this issue by employing first-principles calculations to compare the structural, electronic and electrochemical properties of two common MXenes, namely $Ti_3C_2T_2$ and V_2CT_2, with both uniform terminating groups and explicitly mixed terminations [1]. The sodium storage capacity and volume change during sodiation in the interlayer space of these MXenes with mixed surface terminations are also investigated.

The redox reaction is shown to be confined to the terminating groups for low concentrations of intercalated Na, with the oxidation state of the metal atoms unaffected until higher concentrations of intercalated Na are achieved. The average open circuit voltage is shown to be very similar for both $Ti_3C_2T_2Na$ and V_2CT_2Na with mixed terminations, although it is highly sensitive to the particular composition of the terminating groups.

We also investigate the intercalation of Al^{3+} ions into $Ti_3C_2T_x$ and V_2CT_x. The three-electron redox capability of Al means such systems could become promising alternatives to Li-ion batteries [2]. We determine how such multi-valent ions interact with the MXene terminating groups, particularly those including fluorine, and discuss how this influences the total capacity of MXene electrodes.

References

[1] Caffrey, Nanoscale, 10 (2018) 13520.
[2] VahidMohammadi, Hadjikhani, Shahbazmohamadi, Beidaghi, ACS Nano, 11 (2017) 11135

Figures

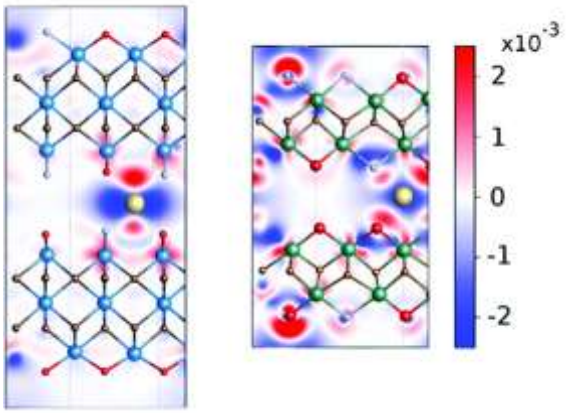

Figure 1: Charge density difference plots for (left) 0.11 ML Na in mixed terminated Ti3C2Tx and (right) 0.11 ML Na in mixed terminated V2CTx.