

MULTIVALENT BATTERIES

Vacancies for reversible insertion

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Rechargeable batteries based on multivalent ions such as Mg^{2+} and Al^{3+} offer an attractive alternative to Li-ion batteries, because these ions are more Earth-abundant and have the ability to transfer more electrons than Li^+ . However, the development of multivalent batteries has been largely hindered by the difficulty in intercalation or deintercalation of the multivalent ions into the electrodes, which is due to the strong electrostatic interactions between these ions and their hosts. Now, Peter Strasser, Damien Dambournet and colleagues design cation-deficient anatase TiO_2 , enabling reversible insertion of Mg^{2+} and Al^{3+} .

The researchers fabricate anatase TiO_2 electrodes with high concentrations of Ti vacancies (22%) through the partial substitution of Ti cations by monovalent anions such as fluoride and hydroxide groups. The introduction of these anions charge-compensate for the creation of the Ti cations, making the resultant compounds stable. Using a comprehensive set of techniques such as high-energy X-ray and NMR, the researchers show that the number of Mg^{2+} ions that can be reversibly intercalated matches the concentration of the Ti vacancies, and the discharge capacity matches the number of inserted Mg^{2+} ions, indicating a two-electron redox reaction mechanism. In a three-electrode cell, which is useful for understanding how battery materials behave under operando conditions, the vacancy-rich anatase TiO_2 electrodes display approximately six times higher discharge capacity (155 mAh g^{-1}) than the stoichiometric anatase TiO_2 .

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