

Intrinsic Voltage Limit and Crystal Field Splitting in Silicate Cathode Materials for Li-Ion Batteries

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The current needs to overcome our dependence on the fossil fuels have drawn a growing interest to the development of more advanced energy storage systems. Among them, rechargeable Li-ion batteries have been the focus of numerous experimental and theoretical studies. The two key properties to characterize the energy density of a Li-ion battery electrode are the specific capacity and voltage of operation. While the specific capacity theoretical limit is given by the chemical formula of the different compounds, the voltage depends on the morphology, relative stability and other electronic properties of the electrode material. In our study, we have focused our attention in polyoxyanion silicates as positive electrode materials. These materials incorporate transition metals (TM) in the host structures to allow the necessary electronic conductivity for the open circuit of the battery, and their voltage is mainly due to the redox activity of these TM. There is always an intrinsic [1] voltage limit for every TM redox couple, and it depends on the position of their electronic d -bands and the hybridization with the anion (oxygen) electronic p -states. In this work, using density-functional theory (DFT) methods, we perform a detailed analysis of the electronic structure of two different silicate morphologies with different redox couples, to find out which is the influence of the crystal structure on the electronic d -bands of the silicate and, by comparing our results with those of regular oxides, to propose mechanisms to control the position of the electronic d -bands and, thus, the voltage and energy density of the Li-ion battery.

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[1] J. B. Goodenough and Y. Kim, Chem. Mater. **22**, 587 (2010).