

## The Charge of Titanium in Titanium Dioxide: $\text{Ti}^{4+}$ Is Not a Tenable Concept

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$\text{TiO}_2$  polymorphs are large-band-gap semiconductors widely used in photocatalysis, solar cells and as electrode materials for Li-ion and Na-ion batteries. Understanding of the mechanism of operation of these technologies relies on understanding of the electronic structure of titania. The oxidation state of titanium in  $\text{TiO}_2$  is commonly assumed to be +4. This is a formal oxidation state based on the ionic approximation. It implies a charge state of +4 and no further oxidation/reduction of Ti/O. This assumption is used ubiquitously to rationalize phenomena observed with  $\text{TiO}_2$ ; for example the assignment of oxidation states obtained in doped  $\text{TiO}_2$  is done off the assumed +4 oxidation state in pure  $\text{TiO}_2$ . The often-cited basis for the assumption of  $\text{Ti}^{4+}$ , photoelectron spectroscopy, relies on qualitative MO considerations to interpret XPS peaks. There does not seem to be direct, independent experimental evidence of the absolute charge state. Ab initio simulations at different levels theory provide different measures (Mulliken, Bader etc) of charge on Ti which are nowhere near +4. For example, Bader charges are on the order of +2.5 e. The band structure of titania compounds was reported extensively, commonly describing the valence band as being primarily composed of O 2p states and the conduction band mostly consisting of Ti 3d contributions. At the same time, the density of states shows other less important contributions, notably from Ti 3d states in the valence band. A recent investigation (Organometallics 36 (2017) 622) using charge reporter molecules concluded that the charge of Ti is close to +3 and highlighted a remarkable stability/similarity of charge states of many transition metal atoms in different environments corresponding to very different formal oxidation states. The evidence is mounting that the concept of  $\text{Ti}^{4+}$  may not be tenable and that the ab initio computed charges very different from +4 may not be a computational fluke but signal a different real charge state.

We present an electronic structure investigation of Ti ions,  $\text{TiO}_2$  molecules and  $\text{TiO}_2$  bulk crystals, using different density functional theory and wave function-based approaches, and in a way which is not dependent on a specific charge definition (such as Mulliken or Bader). We show that there is a significant remaining contribution from valence s and d electrons of Ti, including the presence of a nuclear cusp around the Ti core. The charge corresponding to valence s and d states of Ti amounts to 1e and cannot be assigned to any other atom than Ti. The charge state of Ti in  $\text{TiO}_2$  is therefore near +3. The respective charge state of oxygen would therefore correspond to -1.5. Our results suggest that, in principle, further oxidation of Ti / reduction of O is possible. Further investigations on Ti charge states upon insertion in a variety of crystals, Ti charges in titanium halides as well as charges in titanium carbonyl complexes also confirm the similarity of the Ti charge in different environments. A substantial charge remainder on titanium is predicted for these compounds as well. These results are in agreement with estimates which utilized ligands as charge distribution reporters. We conclude that the charge state of Ti in  $\text{TiO}_2$  is about +3 and the idea of  $\text{Ti}^{4+}$  should be ditched.