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An alternative view on the electrochromism of Ni-deficient nickel oxide

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The escalating global energy demand and its environmental ramifications necessitate swift advancements in renewable energy solutions. A comprehensive understanding of the mechanisms governing sustainable energy systems is imperative for further advancement. A key concern is the substantial energy usage in residential and commercial buildings for heating and cooling purposes. Addressing this challenge, innovative applications are emerging, focusing on electrochromic (EC) materials [1]. These materials can reversibly switch between transparent (bleached) and coloured states upon the application of a DC voltage. EC materials encompass metal oxides, conductive polymers, and inorganic non-oxides blended with ionic and electronic conductors. Nickel oxide (NiO) is one of the best-known EC materials. While the exact mechanism of EC in NiO is discussed for a long time, it is generally considered that in hydrated nickel oxide, particularly focusing on color changes in Li^+-containing electrolytes. One of the proposed mechanism involves transition between transparent $Li^{+}{}_{2x}Ni^{2+}{}_{(1-x)}O^{2-}$ and colored $Li^{+}{}_{(2x-y)}Ni^{2+}{}_{(1-x-y)}Ni^{3+}{}_{y}O^{2-}$, following the reaction $Li^{+}{}_{2x}Ni^{2+}{}_{(1-x)}O^{2-} \leftrightarrow Li^{+}{}_{(2x-y)}Ni^{2+}{}_{(1-x-y)}Ni^{3+}{}_{y}O^{2-} + yLi^{+} + ye^{-}$ [2]. In the present work, through DFT+U calculations, we investigated the electrochromism of Ni-deficient NiO and found a new mechanism distinct from the conventional view associating optical spectra changes solely with variations in Ni^{2+}/Ni^{3+} oxidation states [3]. First, considering bulk NiO, our results reveal the formation of a hole bipolaron in Ni-deficient NiO, with Li insertion filling one hole state, leaving one-hole polaron in the system. Consequently, electronic structure alterations directly impact optical spectra, resulting in reduced absorption coefficients in Li-intercalated NiO compared to initial Ni-deficient NiO (Figure 1, a). Interestingly, we observed minimal changes in Ni oxidation states during Li insertion, indicating a general process where hole bipolaron states are filled by adding a single electron, largely independent of specific positive counter ions. Our findings, supported by results with Li^+, Na^+, and K^+ ion insertion in Ni-deficient NiO(001) surface, suggest a broader applicability of this mechanism, potentially explaining NiO electrochromism observed across various electrolytes beyond Li-containing ones, as well as doped NiO-based materials where the distortion of the NiO lattice by dopants could lead to more efficient stabilization of polaronic structures.

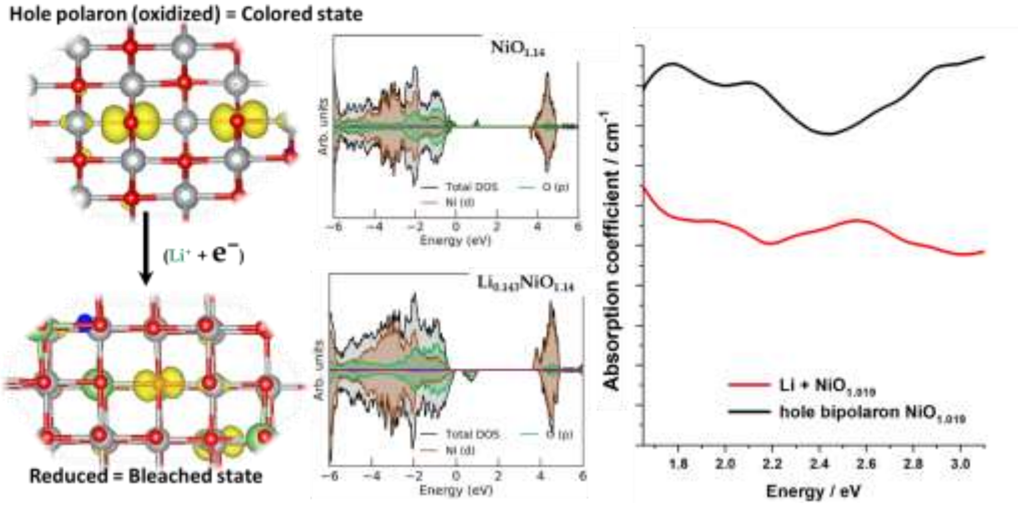

Figure 1. Electronic structure and optical spectra changes upon (Li^++e^-) insertion in Ni-deficient NiO bulk

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