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Lanthanum Based Perovskites Exhibiting Hydroxide Ion Storage for Pseudocapacitor Electrodes

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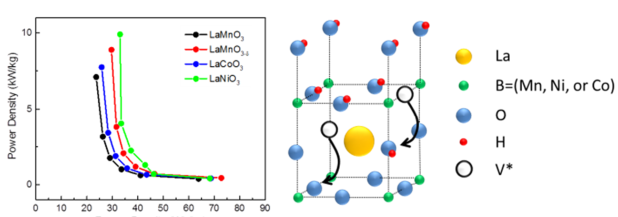
Metal oxides have gained significant interest as pseudocapacitor electrodes due to reversible faradaic surface reactions that allow for high power density and greater energy storage than carbon based electric double layer capacitors. However, classically investigated materials like RuO_2, MnO_2, and $Ni(OH)_2$ suffer from high cost, low life cycles, or limited potential windows, respectively.[1-3] As such, there is growing demand for new materials with improved energy storage and stability. Herein, we demonstrate the capacitive characteristics of three lanthanum based perovskite type oxides, $LaMnO_3$, $LaNiO_3$, and $LaCoO_3$. Based on the inherent nature of perovskites to contain oxygen vacancies, we demonstrate through cyclic voltammetry that perovskites store charge through anions in alkaline electrolytes, likely in the form of hydroxides. This hypothesis was tested by inducing extrinsic oxygen vacancies in $LaMnO_3$ through a low temperature reduction in H_2/Ar. It was found that substoichiometric $LaMnO_{3-\delta}$ exhibits ~20% greater capacitance, highlighting the significance of oxygen vacancies as charge-storage sites in these perovskite type oxides. Importantly, due to the well-known oxide and proton ionic conduction characteristics of perovskites, we demonstrate that charge storage is not limited to the surface of these materials. Rather, it may extend into the bulk of the structure, leading to higher energy storage than traditional psuedocapacitors which are inherently limited by surface confined reactions. As the first study of these materials for pseudocapacitor applications, only moderate structural and electrochemical optimizations have been carried out. As such, the high specific capacitances of >500F/g and high cycling stability for the materials of this study imply a promising future for perovskite structured pseudocapacitors.



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