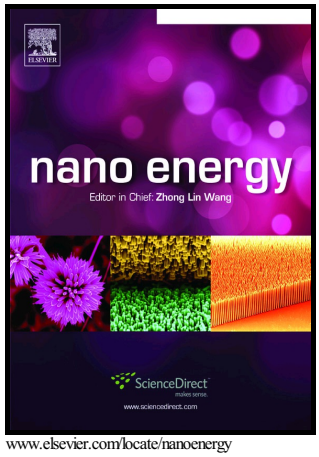

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PII: S2211-2855(18)30642-6
DOI: https://doi.org/10.1016/j.nanoen.2018.09.005
Reference: NANOEN3010

To appear in: *Nano Energy*

Received date: 25 April 2018
Revised date: 31 August 2018
Accepted date: 1 September 2018

Cite this article as: Sanja Tepavcevic, Justin G. Connell, Pietro P. Lopes, Mukesh Bachhav, Baris Key, Carlos Valero-Vidal, Ethan J. Crumlin, Vojislav R. Stamenkovic and Nenad M. Markovic, Role of Structural Hydroxyl Groups in Enhancing Performance of Electrochemically-Synthesized Bilayer V_2O_5, *Nano Energy,* https://doi.org/10.1016/j.nanoen.2018.09.005

Role of Structural Hydroxyl Groups in Enhancing Performance of Electrochemically-Synthesized Bilayer V_2O_5

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Abstract

Nanostructured electrode materials represent a promising path forward to dramatically improving the performance of both Li-ion and beyond Li-ion battery systems; however, difficulties in characterizing the structural and electrochemical changes that take place in nanoscale systems, which are often poorly crystalline or amorphous, make it difficult to develop design rules for synthesizing new materials with optimal performance. Bilayered vanadium oxide-based materials (BL-V_2O_5) are an ideal platform for understanding the underlying physicochemical properties that determine capacity in nanomaterials, with electrochemically-synthesized V_2O_5 (EC-V_2O_5) exhibiting particularly high capacities. In this work we provide evidence that the source of high practical capacity in EC-V_2O_5 is the presence of "structural hydroxyl groups" that are an intrinsic feature of the electrochemical synthesis method. Using both *in situ* and *ex situ* characterization methods, we demonstrate that structural OH species are highly stable and persist in the structure during reversible cycling. We hypothesize three important roles for structural OH groups: they maintain a sufficient interlayer spacing to allow the physical diffusion of cations over multiple cycles; they maintain a consistent solvating environment in the bilayer regardless of structural H_2O content; and they reduce the symmetry of vanadium polyhedra to favor electron transfer over pseudocapacitive adsorption, making it possible to access close to theoretical capacity. These insights have broad implications for understanding the performance of a variety of hydrated oxide systems, and indicate that the formation of covalently-bound hydroxyoxide species can lead to further improvements in the performance of nanoscale materials.