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Influence of Vanadium Doping on Electrochemical Performance of Nickel Oxide in Supercapacitors

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1. Supplementary Results

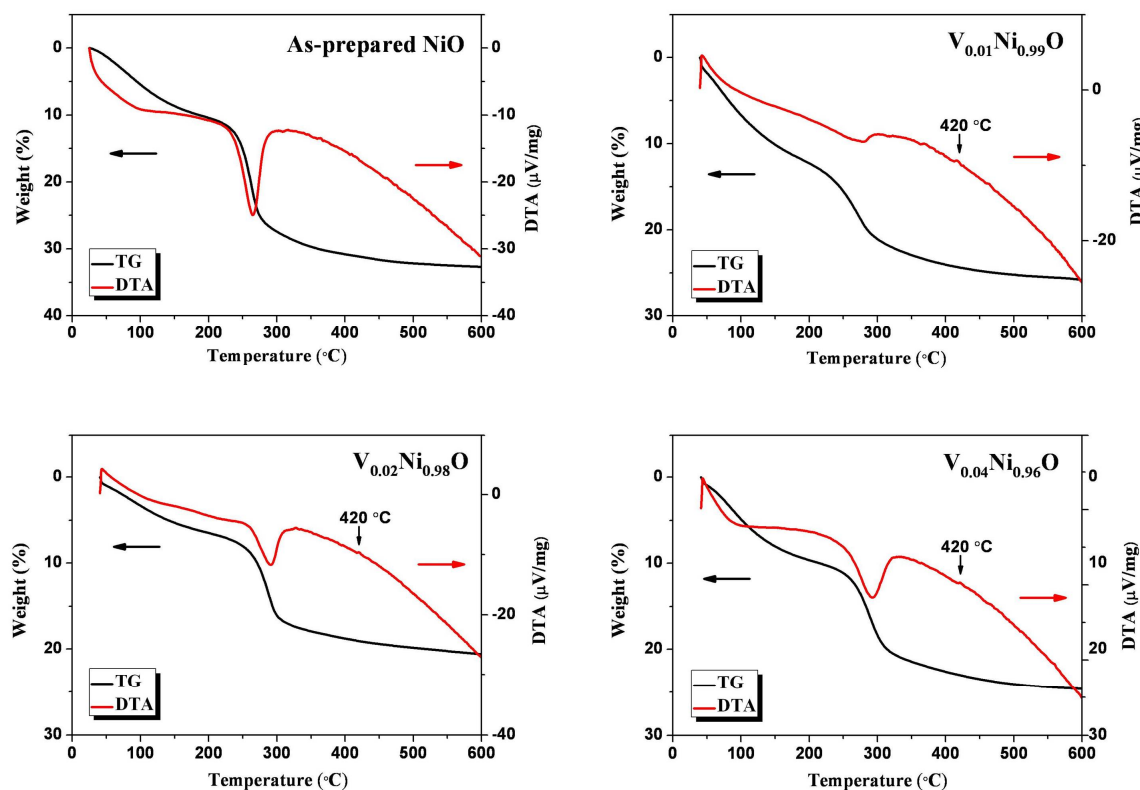


Fig. S1. TG-DTA curves of as-prepared NiO and V-doped NiO samples.

For the mixed oxides (Ni-V oxides), the calcinated temperature could be affected by its kinetics of the oxidation of electrode, which is composed of NiO and VO_x . From TG-DTA curves (**Fig. S1**), the major weight loss at about 260 and 290 °C for the pure NiO and V-doped NiO, respectively, corresponds to the peak position in DTA curves. For all V-doped NiO samples, a weak and slight exothermic peak related to vanadium oxide is observed at about 420 °C.²⁴ (T. Watanabe et al., *J. Mater. Chem.*, 1995, **5**, 753) Some papers also reported that vanadium oxide species (V_2O_3 , VO_2 and V_2O_5) were prepared by the calcination temperature (> 400 °C). (K. Takahashi et al., *J. Phys. Chem. B*, 2004, **108**, 9795; O. Merdignac-Conanec et al., *J. Solid State Chem.*, 2005, **178**, 218; Y. Zhang et al., *Mater. Res. Bull.*, 2012, 47, 1978) O. Merdignac-Conanec et al. and Y. Zhang et al. reported that vanadium oxide species were crystallized at 450 °C as orthorhombic V_2O_5 shcherbinaite with

loss of fibrous structure corresponding to the oxidation of the bulk VO_2 to V_2O_5 , as represented in following Eq: $4\text{VO}_2 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5$. Layered V_2O_5 -like materials show the typical redox intercalation ability for various intercalating species. Moreover, the electrochemical K^+ insertion process occurring at V_2O_5 electrodes can be expressed as $\text{V}_2\text{O}_5 + x\text{K}^+ + xe^- \leftrightarrow \text{K}_x\text{V}_2\text{O}_5$. Therefore, it is important that vanadium species are formed as V_2O_5 (vanadium oxidation state : +5). This is because V_2O_5 is more stable and more excellent electrochemical performance than other vanadium oxide species (V_2O_3 and VO_2) for pseudocapacitors. Hence, we choose the 500 °C as the calcine temperature to form V_2O_5 with fully oxidation of vanadium species and the decomposition of various organic moieties.

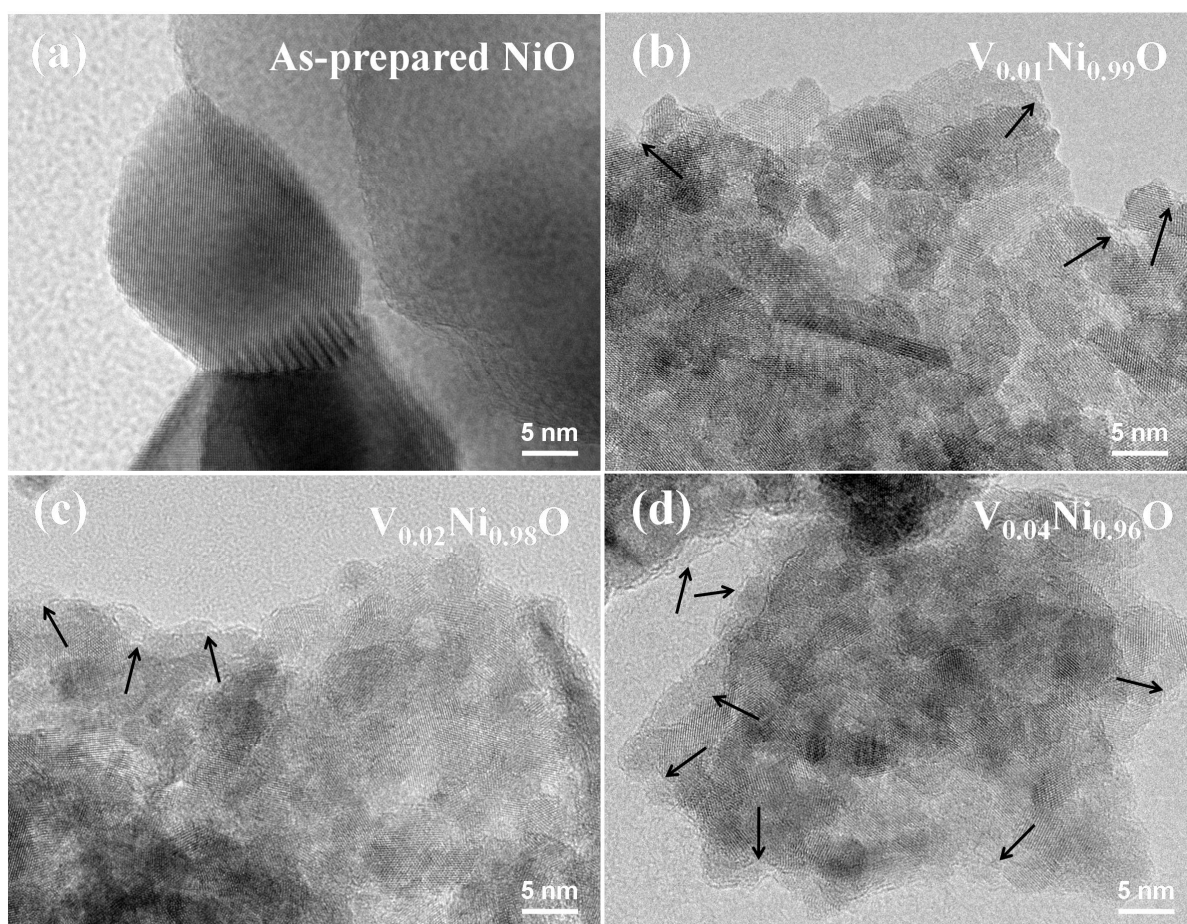


Fig. S2. TEM images of as-prepared NiO and V-doped NiO samples.

The oxidation state of vanadium oxide (from V^{5+} to V^{4+}) decreased as the at.% of V increased. This indicates that a result of the partial reduction of some V^{5+} to V^{4+} in $\text{V}_x\text{Ni}_{1-x}\text{O}$

samples, resulting structural disorder due to the percolation of V on the surface of NiO or the NiO lattice. Through the heat treatment, the percolated V on the surface of NiO or the NiO lattice formed the passivation layer on the surface of NiO. (**Fig. S2b, c, d**) This passivation layer and its thickness, for vanadium dioxide (VO_2 , V^{4+}) associated with semiconducting behavior, functioned as leading to low carrier density, resulting large increase of the resistivity under 67 °C. (*S.A. Corr et al., Chem. Mater.*, 2008, **20**, 6396; C. Chen et al., *J. Appl. Phys.*, 2011, **110**, 023707)

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