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

Hae Woong Park, a Byung-Ki Na, b Byung Won Cho, c Sun-Min Park a and Kwang Chul Roh* a

a Energy Efficient Materials Team, Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, 233–5 Gasan-dong, Guemcheon-gu, Seoul 153-801, Republic of Korea. Fax: +82 2 3282 2475; Tel: +82 2 3282 2463; E-mail: rkc@kicet.re.kr

b Department of Chemical Engineering, Chungbuk National University, 52 Naesudong-ro, Heungdeok-gu, Cheongju, Chungbuk 361-763, Republic of Korea

c Center for Energy Convergence, Korea Institute of Science and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, Republic of Korea

* Corresponding author: E-mail address: rkc@kicet.re.kr (K.C. Roh)
1. Supplementary Results

![TG-DTA curves of as-prepared NiO and V-doped NiO samples.](image)

**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$_2$O$_3$, VO$_2$ and V$_2$O$_5$) were prepared by the calcination temperature (> 400 °C). (K. Takahashi et al., J. Phys. Chem. B, 2004, 108, 9795; O.Merdrignac-Conanec et al., J. Solid State Chem., 2005, 178, 218; Y. Zhang et al., Mater. Res. Bull., 2012, 47, 1978) O. Merdrignac-Conanec et al. and Y. Zhang et al. reported that vanadium oxide species were crystallized at 450 °C as orthorhombic V$_2$O$_5$ shecherbinaite with...
loss of fibrous structure corresponding to the oxidation of the bulk VO_{2} to V_{2}O_{5}, as represented in following Eq: 4VO_{2} + O_{2} \rightarrow 2V_{2}O_{5}. Layered V_{2}O_{5}-like materials show the typical redox intercalation ability for various intercalating species. Moreover, the electrochemical K^{+} insertion process occurring at V_{2}O_{5} electrodes can be expressed as V_{2}O_{5} + xK^{+} + xe^{-} \leftrightarrow K_{x}V_{2}O_{5}. Therefore, it is important that vanadium species are formed as V_{2}O_{5} (vanadium oxidation state : +5). This is because V_{2}O_{5} is more stable and more excellent electrochemical performance than other vanadium oxide species (V_{2}O_{3} and VO_{2}) for pseudocapacitors. Hence, we choose the 500 °C as the calcine temperature to form V_{2}O_{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 (form 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 V_{x}Ni_{1-x}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)

References


