# Nitridation of titanate nanoparticles and their electrochemical properties

Tateki Kiyo[1], Tomoki Tsumura[1,*], Taro Kinumoto[1], Shiro Shimada[3], Hajime Kiyono[3], Osamu Tanaike[2], Masahiro Toyoda[1]

*Oita University[1], National Institute of Advanced Industrial Science and Technology[2], Hokkaido University[3]*

*Oita University, 700 Dannoharu, Oitasi, Oita 870-1192, Japan*

**Tel: +81-97-554-7912, Fax: +81-97-554-7912, E-mail: ttsumura@cc.oita-u.ac.jp*

**Abstract**

Titanate nanoparticles (TNPs) synthesized under hydrothermal condition were nitrided under $NH_3$ gas flow. N-doped $TiO_2$ anatase ($TiO_xN_y$) was formed at between 800 and 950 $^oC$ for 1 h and O-contained TiN ($TiN_{x'}O_{y'}$) was formed at 950 $^oC$ for 2 h. Both $TiO_xN_y$ and $TiN_{x'}O_{y'}$ showed an electrochemical lithium ion insertion/extraction reaction but their capacity decreased with the increase of N/Ti ratio. $TiN_{x'}O_{y'}$ showed the highest retention ratio of charge capacity at 1000 mA $g^{-1}$ to that at 40 mA $g^{-1}$ of 60 %.

## Introduction

Titanium oxides have been studied as electrode materials for lithium-ion batteries and capacitors and recently have attracted attention from a safety and reliability standpoint because of its higher reaction potential than that of cathodic decomposition of electrolyte. On the other hand, an electric conductivity of titanium oxides is so poor that its capacity for rapid charge/discharge usage becomes small. Therefore improvement of the rate performance is remaining an important issue.

Conductivity of titanium oxide can be improved by nitridation. Oxygen atoms in the oxides are able to be replaced nitrogen atoms to some extent without structural change and then semiconducting titanium oxide changes to titanium nitride with metallic conductivity above threshold of nitrogen doping level.

In the present study, titanate nanoparticles (TNPs) were nitrided at different temperatures to prepare titanium oxides with different nitrogen doping level and effect of the nitridation level on electrochemical properties was investigated.

## Experimental

TNPs were synthesized under hydrothermal condition. 5 g of $TiO_2$ (P 25, Degussa Co. Ltd.) and 0.047 $dm^3$ of 8 M KOH aq. solution were put into a tetrafluoroethylene-lined stainless steal vessel and then heated at 150 $^oC$ for 20 h. TNPs

were obtained by rinsing the naturally-cooled product with 0.1 M HCl aq. solution and distilled water for several times, followed by drying at 110 $^{o}$C. Nitridation of TNPs was carried out by heating at 800, 850, 900 and 950 $^{o}$C under high-purity $NH_3$ gas flow.

Charge-discharge test was performed by using two-electrode cell. The sample was mixed with carbon black and polyvinylidene fluoride dissolved in n-methyl pyrolidinone with a mass ratio of 8:1:1 to get a slurry. The slurry was coated on nickel mesh and dried at 120 $^{o}$C under vacuum to make a working electrode. Lithium foil was used as a counter electrode. The electrolyte was 1 M $LiBF_4$ EC/DEC (1:1 by volume) solution. Rate performance was investigated by charging and discharging in the voltage range between 1.2 and 3.0 V with different constant current densities, 40, 100, 400, and 1000 mA $g^{-1}$.

## Results and Discussions

Morphology of TNPs nitrided at below 850 $^{o}$C was nanofiber with 30 ~ 40 nm in diameter, but TNPs nitrided at above 900 $^{o}$C were nanoparticles with the size of around 60 nm. All TNPs nitrided had $TiO_2$ anatase type structure except for TNPs heated at 950 $^{o}$C for 2 h (TNP-950-2 h). TNP-950-2 h consisted of titanium nitride with rock salt type structure. From XPS analysis, nitrogen was detected for the sample nitrided at above 850 $^{o}$C and nitrogen content increased with the increase of nitridation temperature. N/Ti ratio of TNP-950-2 h being 0.64, TNP-950-2 h might contain significant oxygen in its structure. From these results, the nitrided samples with anatase and rock salt type structure were expressed as $TiO_xN_y$ and $TiN_{x'}O_{y'}$ ,respectively.

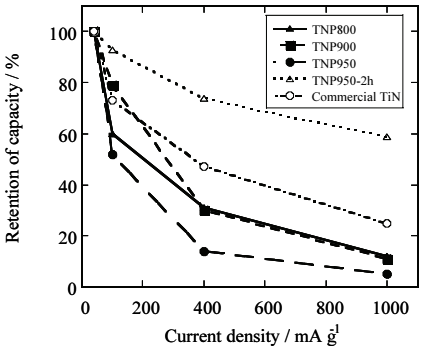


Fig. 1 Retention capacity of commercial TiN and TNPs nitrided at different temperatures under high-purity $NH_3$ gas flow.

Fig. 1 shows rate performance of the samples, retention rate of the charge capacity at 40, 100, 400, and 1000 mA $g^{-1}$ to that at 40 mA $g^{-1}$ being plotted. For all the samples, with the increase of the current density, the capacity decreases. Retention rate at 1000 mA $g^{-1}$ of TNP-950-2 h is 60 %, but that of other nitrided samples is below 15 %. However, charge capacities at 40 mA $g^{-1}$ of TNP-800, -900, -950 and -950-2 h were 118, 100, 85 and 27 mAh $g^{-1}$, respectively.

## Conclusions

Titanate nanoparticles (TNPs) were nitirided at above 850 $^{o}$C under $NH_3$ gas flow. TNPs nitrided at 950 $^{o}$C for 2 h had $TiN_{x'}O_{y'}$ rock salt type structure and showed the highest retention rate of capacity at 1000 mA $g^{-1}$ of 60 %.