

## Electronic Supplementary Information

# Nano-structured ternary niobium titanium nitrides as durable non-carbon supports for oxygen reduction reaction

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## Methods

**Synthesis of oxides.** The alkali titanoniobates  $\text{KTiNbO}_5$  and  $\text{KTi}_3\text{NbO}_9$  were synthesized by solid-state reaction of stoichiometric mixtures consisting of  $\text{K}_2\text{CO}_3$  (anhydrous powder, 99.99%, Aldrich),  $\text{TiO}_2$  (99.99%, Aldrich), and  $\text{Nb}_2\text{O}_5$  (99.99%, Aldrich) powders in the molar ratios 1:2:1 and 1:6:1, respectively. After grinding, stoichiometrically mixing, and pelletizing the commercially-available and high-purity powders, the 1.0 g pellets were placed in Pt boats. The  $\text{KTiNbO}_5$  mixture was heated at a temperature of 1150 °C for 24 h, and the  $\text{KTi}_3\text{NbO}_9$  mixture was heated at 1300 °C for 24 h. The phase purity of the resulting compounds was confirmed by PXRD.

**Synthesis of nitrides.** A series of ammonolysis reactions were done using  $\text{KTiNbO}_5$  and  $\text{KTi}_3\text{NbO}_9$  precursors: 8-hour reactions at temperatures of 500, 600, 700, and 800 °C. These reactions were prepared as follows. Approximately 0.5 g of precursor was placed in an alumina boat, and the boat was placed in a stainless steel tube with airtight, stainless steel end-caps that have welded valves and connections to input and output gas lines. The stainless steel tube was then placed in a split tube furnace, and appropriate connections were made to gas sources containing gases purified to remove trace

amounts of oxygen or water using pellet copper, nickel, palladium, and platinum on zeolite supports. An argon gas flow through the tube was then used for 15 min to expel air remaining in the tube, and the ammonia gas (Anhydrous, Airgas) flow through the tube was subsequently commenced at a flow rate of 200 cm<sup>3</sup>/min. Next, the sample was heated in the tube to the desired reaction temperature at a rate of 150 °C/h. After 8 h elapsed at the desired temperature, the furnace power was turned off and the product was cooled to room temperature in approximately 4 h under an ammonia gas flow. An argon gas flow was then used to purge the tube of ammonia gas before removal of the gas connections. After removing a tube from the furnace, it was left on a lab bench for 24 h with one valve open so that the ammonolysis product could be exposed to air slowly. The product was then washed with DI water to remove any K-containing byproducts, if present.

**Preparation of catalysts.** The Pt/Nb<sub>0.5</sub>Ti<sub>0.5</sub>N, Pt/Nb<sub>0.25</sub>Ti<sub>0.75</sub>N and Pt/carbon black (Vulcan XC-72) catalysts were prepared by a polyol process with ethylene glycol (EG) as a reducing agent.<sup>1</sup> The total Pt loading on each support was 20 wt%. Appropriate amounts of H<sub>2</sub>PtCl<sub>6</sub> (99.995%, Sigma-Aldrich) and the support were suspended in 50 mL of EG solution. This solution was sonicated for 30 min., then transferred to a 100 mL round-bottom, three-neck flask. EG was used to fill this 100 mL flask to approximately 2/3 capacity. Next, the mixture was heated and stirred at 140 °C for 3 h. The resulting suspension was filtered and washed with DI water, then dried in an evacuated desiccator at room temperature to obtain the Pt/Nb<sub>0.5</sub>Ti<sub>0.5</sub>N, Pt/Nb<sub>0.25</sub>Ti<sub>0.75</sub>N and Pt/C catalysts.

**Analysis.** Oxides and nitrides were ground into fine powders and then analyzed with a Rigaku Ultima VI powder X-ray diffractometer with Cu K radiation (K<sub>α1</sub>, λ = 1.5406 Å and K<sub>α2</sub>, λ = 1.5444 Å). Phase purity and crystal structures were confirmed by powder X-ray diffraction profiles using the EXPGUI, GSAS package.<sup>2</sup> As previously discussed, the nitride crystalline domain size can be estimated from a Rietveld fit of the Lorentzian function.<sup>3</sup>

Elemental analyses of nitrogen and oxygen content of the nitride samples were done with a LECO TC-600 analyzer using the inert gas fusion method. Nitrogen was detected as N<sub>2</sub> by thermal conductivity and oxygen was detected as CO<sub>2</sub> by infrared detection. The apparatus was calibrated using Leco® standard oxides; Si<sub>2</sub>N<sub>2</sub>O and TaN were used as nitrogen standards.<sup>3</sup>

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were done with a LEO-1550 field emission SEM (FSEM). Approximately 2 mg of the Nb-Ti nitride was dispersed in 2 mL of ethanol. After this solution was sonicated for 30 min., one drop of the solution was transferred by glass pipet onto a TEM copper grid (3.05 mm holey carbon, Sigma-Aldrich). Transmission electron microscopy analysis was done with a FEI T12 Spirit TEM STEM.

Nitrogen adsorption and desorption isotherms to determine specific surface area (m<sup>2</sup>/g) were measured at -196 °C using a Micromeritics ASAP 2020 system. Samples were degassed on a vacuum line at 200 °C for 24 h.

A four-point probe measurement of conductivity of the compressed powders at a pressure of 35 bar was used to estimate the electrical conductivities of compressed Nb-Ti nitride powders.

### ***Electrochemical Measurements***

**Reagents.** All the chemicals used in electrochemical experiments were reagent grade. They included ultra high purity (99.994%) oxygen (Airgas), high purity (99.999%) sulfuric acid (Sigma-Aldrich), and Nafion (5 wt %, Sigma-Aldrich). All solutions were prepared with deionized water purified by a Hydro purification system connected in series to a Millipore Milli-Q system (18 MΩ·cm). Solutions of sulfuric acid were prepared by mixing the concentrated acid into the appropriate volume of water to yield the target molarity.

**Electrochemical Setup and Electrode Cleaning.** Experiments were carried out in a three-chambered electrochemical cell, with compartments separated by medium porosity glass frits, using a 5 mm glassy

carbon working electrode, a Ag/AgCl reference electrode, and a Pt-mesh counter electrode. Rotating disk electrode voltammetry was performed using a Pine Bipotentiostat (Model AFCBP1) and an analytical rotor (Model AFMSRX). The glassy carbon electrode was rotated between 50 and 2000 rpm, with several rotation rates in between, chosen to obtain more reliable Levich plots. RDE data was obtained at 20 mV/s. To use the glassy carbon electrode, it was first manually polished with 1 $\mu$ m Buehler Metadi diamond paste on a Buehler Microcloth polishing cloth, and then it was sonicated in 1.0 M NaOH solution for 15 minutes. Nanoparticles could then be deposited onto the electrode surface. No electrochemical cleaning was performed before the deposition of nanoparticles.

**Electrochemical Equations** In rotating disk electrode (RDE) voltammetry, the number of electrons that are involved in a reduction reaction at a chosen potential can be obtained from the Levich equation:

$$i_{l,c} = -0.62nFAD_R^{2/3} \omega^{1/2} \nu^{-1/6} C_R^*$$

where  $i_{l,c}$  is the limiting cathodic current at a given electrode rotation rate  $\omega$  (rad/s),  $n$  is the number of e- transferred,  $F$  is Faraday's constant,  $A$  is the electrode area (cm<sup>2</sup>),  $D_R$  is the diffusion coefficient of the reduced species (cm<sup>2</sup>/s),  $\nu$  is the kinematic solution viscosity, and  $C_R^*$  is the bulk concentration of the oxidized species (mol/cm<sup>3</sup>). For our analyses of O<sub>2</sub> (aq), we used the diffusion coefficient for O<sub>2</sub> (aq) of  $1.63 \times 10^{-5}$  cm<sup>2</sup>/s for pH = 1 and a concentration of 1.26 mM. The Levich equation is valid when the system is mass-transport-limited at all rotation rates used in the calculation, and this is evidenced by linearity in the Levich plot. Deviations from linearity may indicate some kinetic limitations or decreased dissolved O<sub>2</sub> due to fast rotation rates.

Table S1. Summary of ammonolysis conditions for potassium-containing oxides and resulting phases.

Precursor	Temp. & time	Resulting phase
KNbTiO <sub>5</sub>	500 C, 8h	KNbTiO <sub>5</sub>
	600 C, 8h	KNbTiO <sub>5</sub> , unknown
	700 C, 8h	KNbTiO <sub>5</sub> , unknown
	800 C, 8h	Nb <sub>0.5</sub> Ti <sub>0.5</sub> N
KNbTi <sub>3</sub> O <sub>9</sub>	500 C, 8h	KNbTi <sub>3</sub> O <sub>9</sub>
	600 C, 8h	KNbTi <sub>3</sub> O <sub>9</sub>
	700 C, 8h	KNbTi <sub>3</sub> O <sub>9</sub> , unknown
	800 C, 8h	Nb <sub>0.25</sub> Ti <sub>0.75</sub> N

Figure S1. Powder X-ray diffraction patterns of the K-containing oxides and (Nb<sub>x</sub>Ti<sub>1-x</sub>)N (x = 0.25 and 0.5).

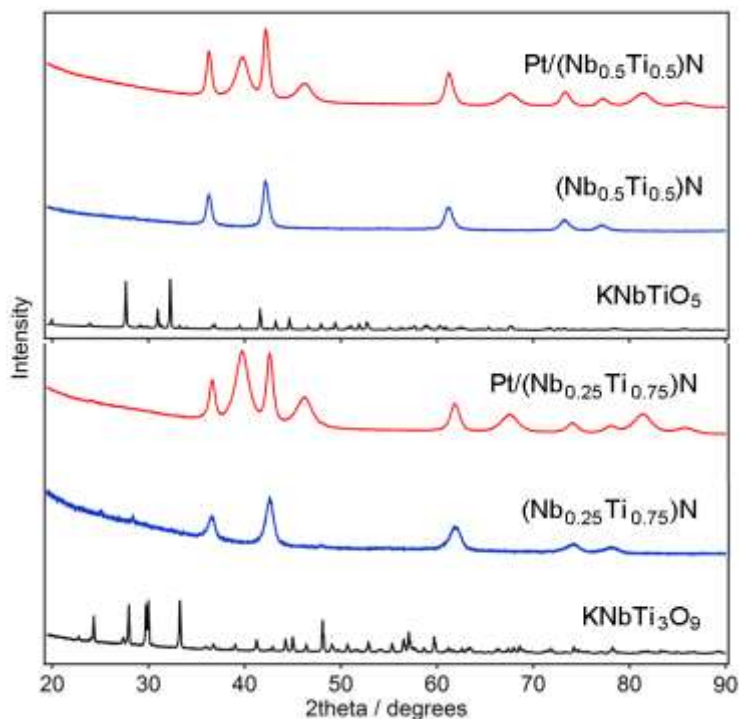


Figure S2. Powder X-ray diffraction patterns of the Pt/C catalyst: \* indicates diffraction peaks for Pt nanoparticle.

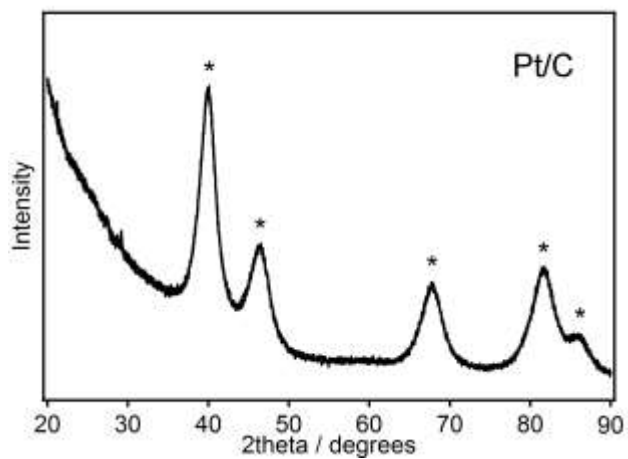
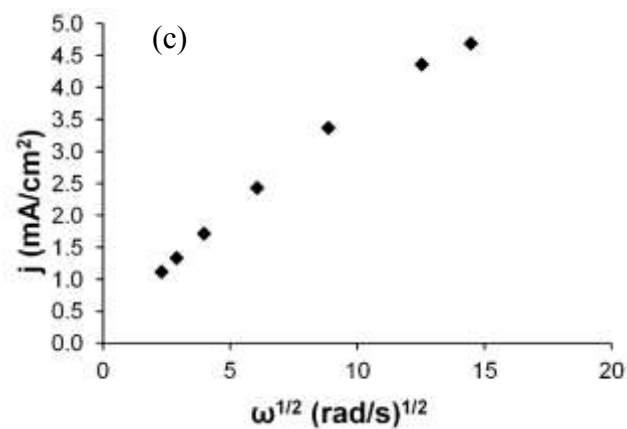
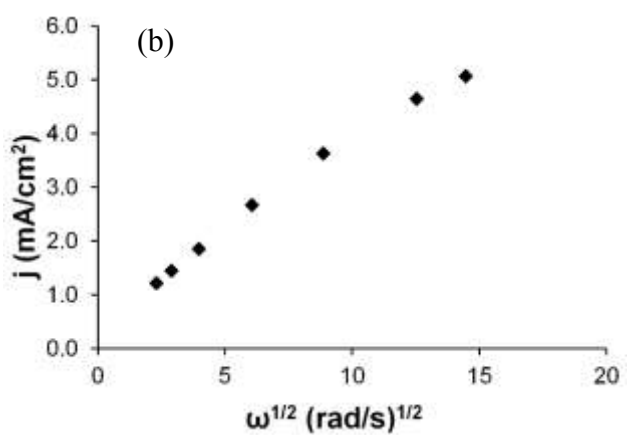
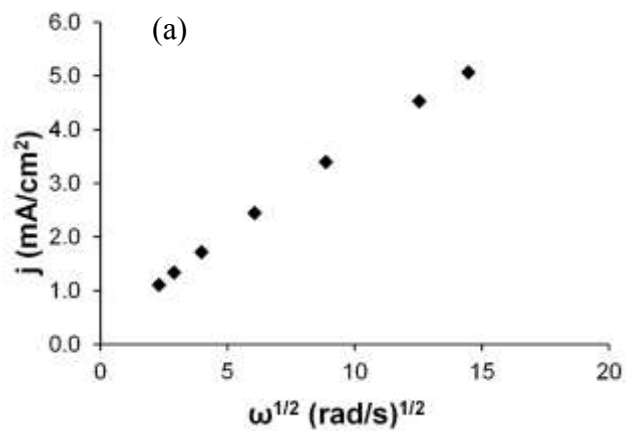


Figure S3. Levich plots for ORR at (a) Pt nanoparticles on glassy carbon, (b) Pt/(Nb<sub>0.25</sub>Ti<sub>0.75</sub>)N on glassy carbon, and (c) Pt/(Nb<sub>0.50</sub>Ti<sub>0.50</sub>)N on glassy carbon.



## References

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