Supplementary information: Effect of Oxidative Surface Treatments on Charge Storage at Titanium Nitride Surfaces for Supercapacitor Applications

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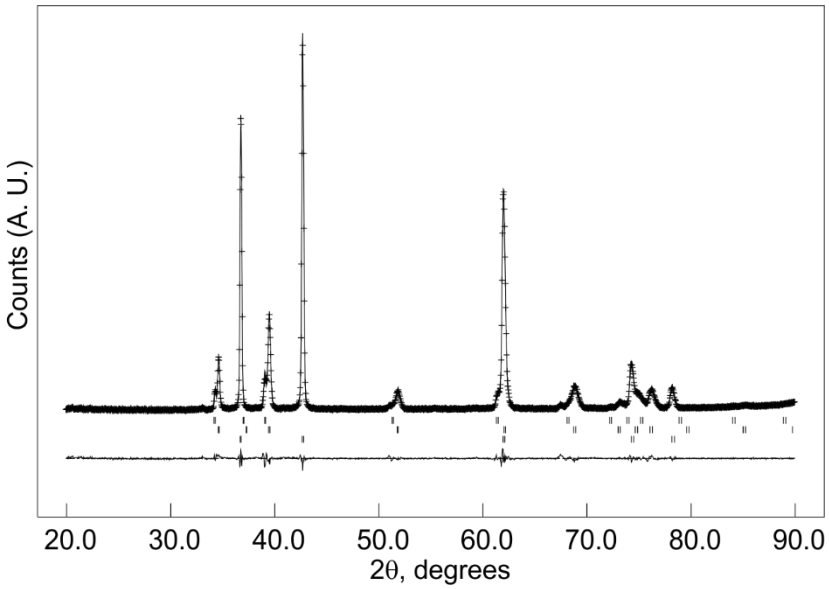

Fig. S1 Model weighted Le Bail fit (R_{wp} = 8.3%, R_p = 5.8%) to the grazing incidence XRD data for a titanium nitride foil with a 5° incidence angle. Crosses mark the data points, the upper continuous line the fit and the lower continuous line the difference. The bottom set of tick marks show the allowed positions of a rocksalt-type (*Fm*-3*m*) TiN phase with *a* = 4.22857(13) Å. The other two sets of tick marks show allowed positions for two hexagonal titanium nitride phases ($P6_3/mmc$) with a = 2.98667(15) and c = 4.8096(4) Å (middle) and a = 3.0191(2) and c = 4.8591(10) Å (top).

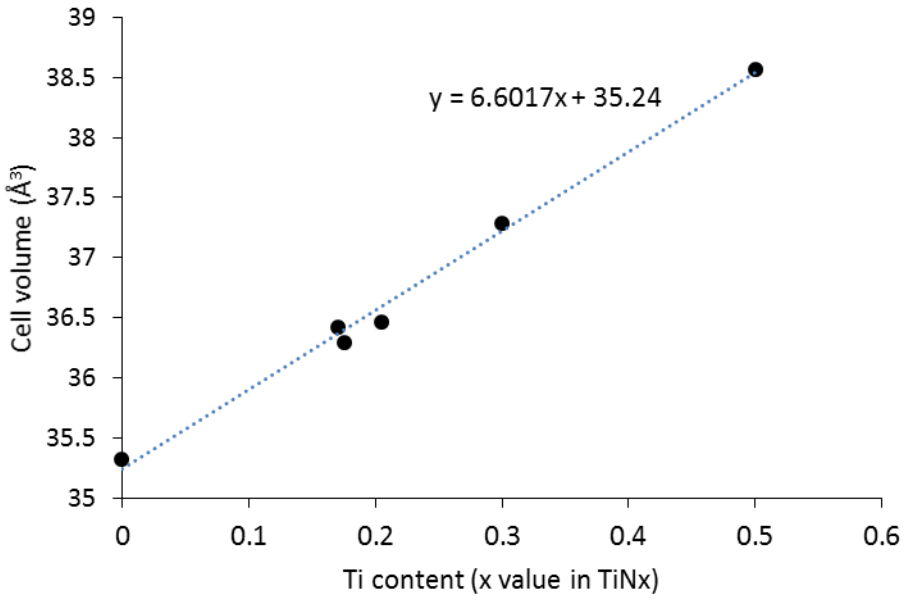

Fig. S2 Graph of cell volume vs nitrogen content in hexagonal titanium nitride phases with the titanium ($P6_3/mmc$) structure, using data from the ICSD and JCPDS databases.[1,2]

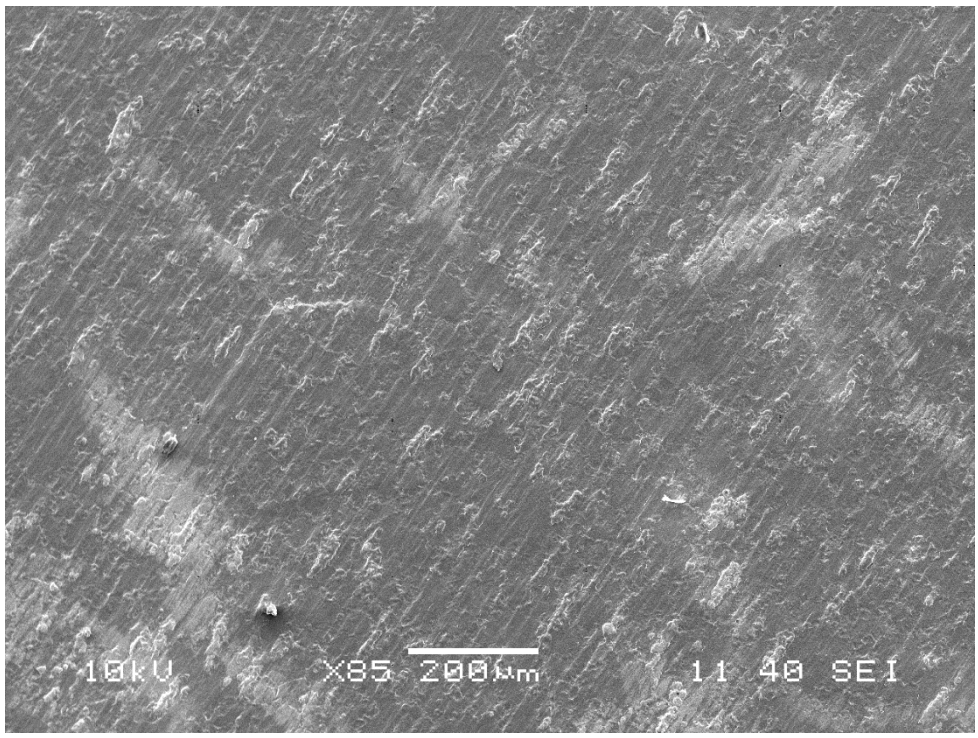

Fig. S3 SEM image of the surface of an as-prepared TiN foil.

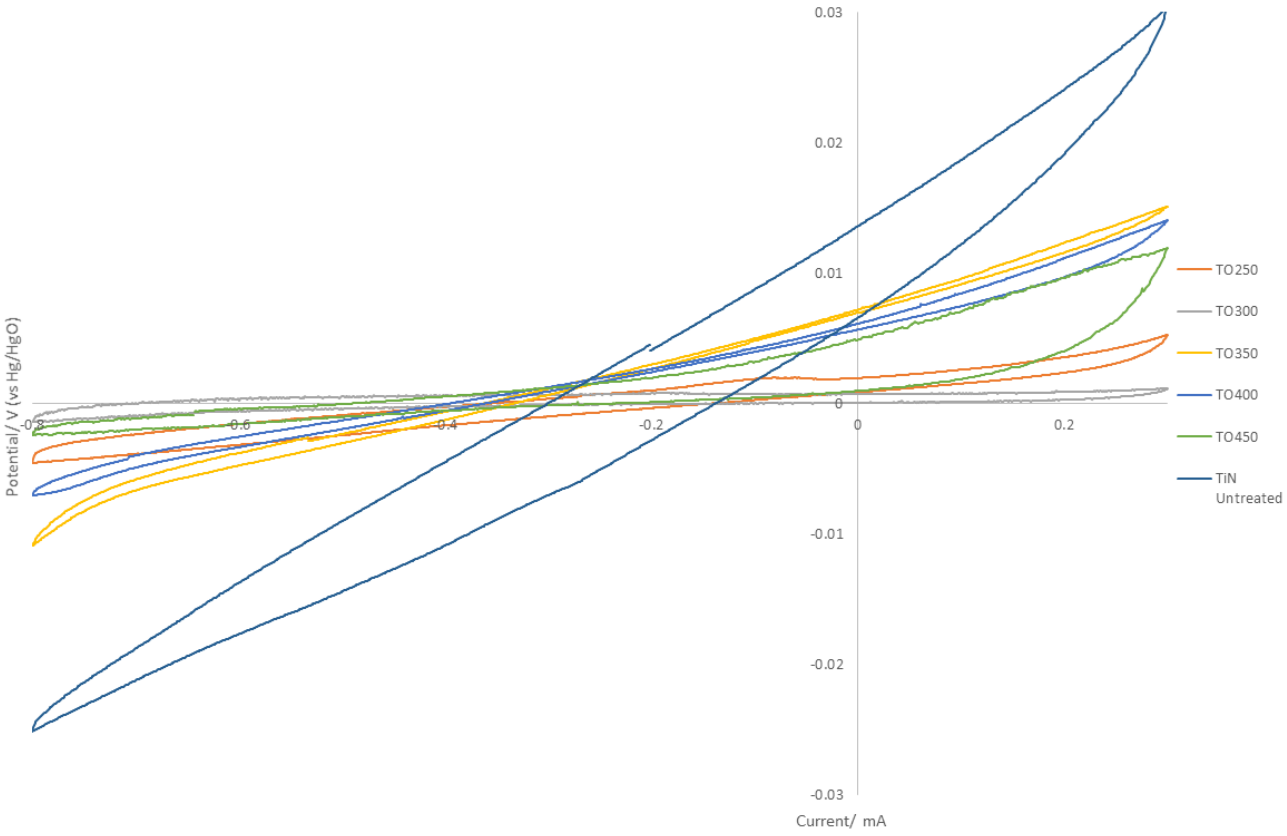

Fig. S4 The 5th CV cycle at 1 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

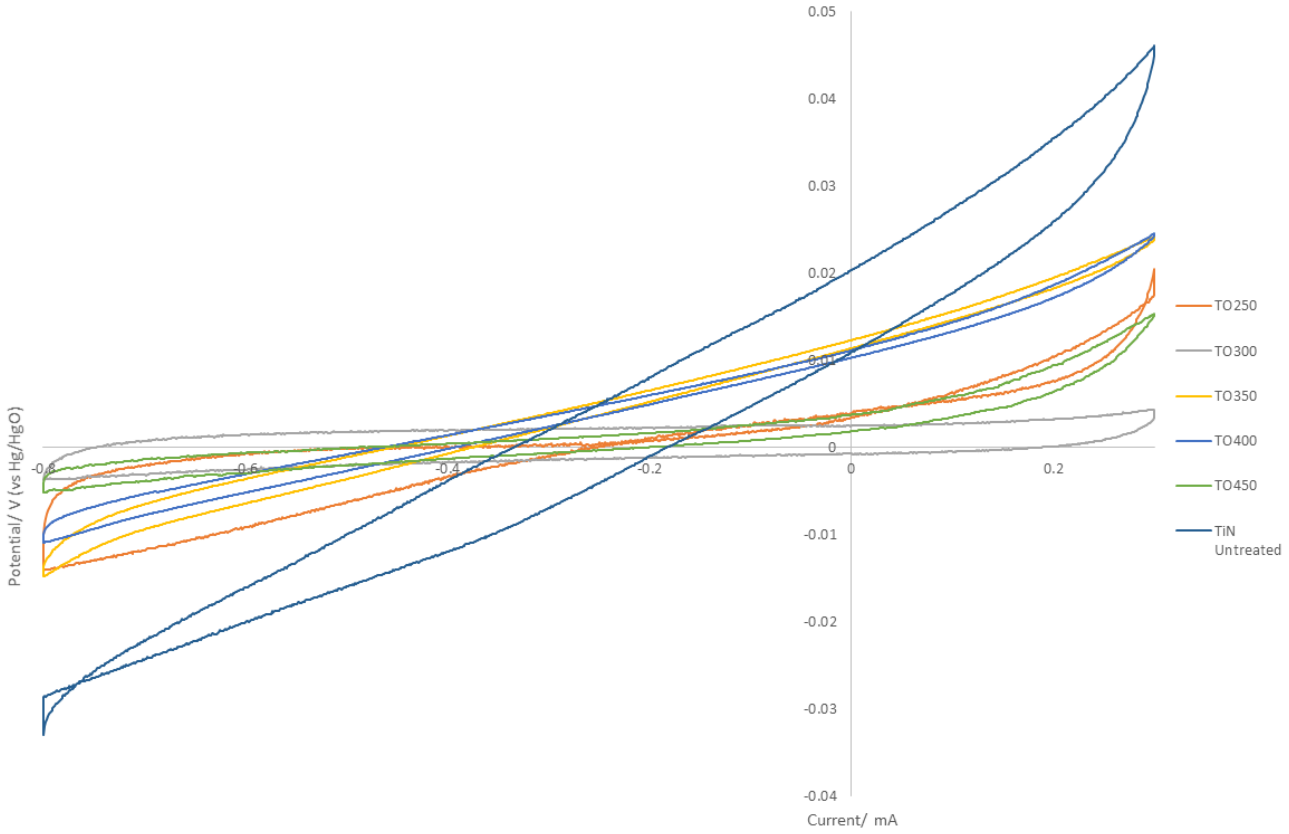

Fig. S5 The 5th CV cycle at 5 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

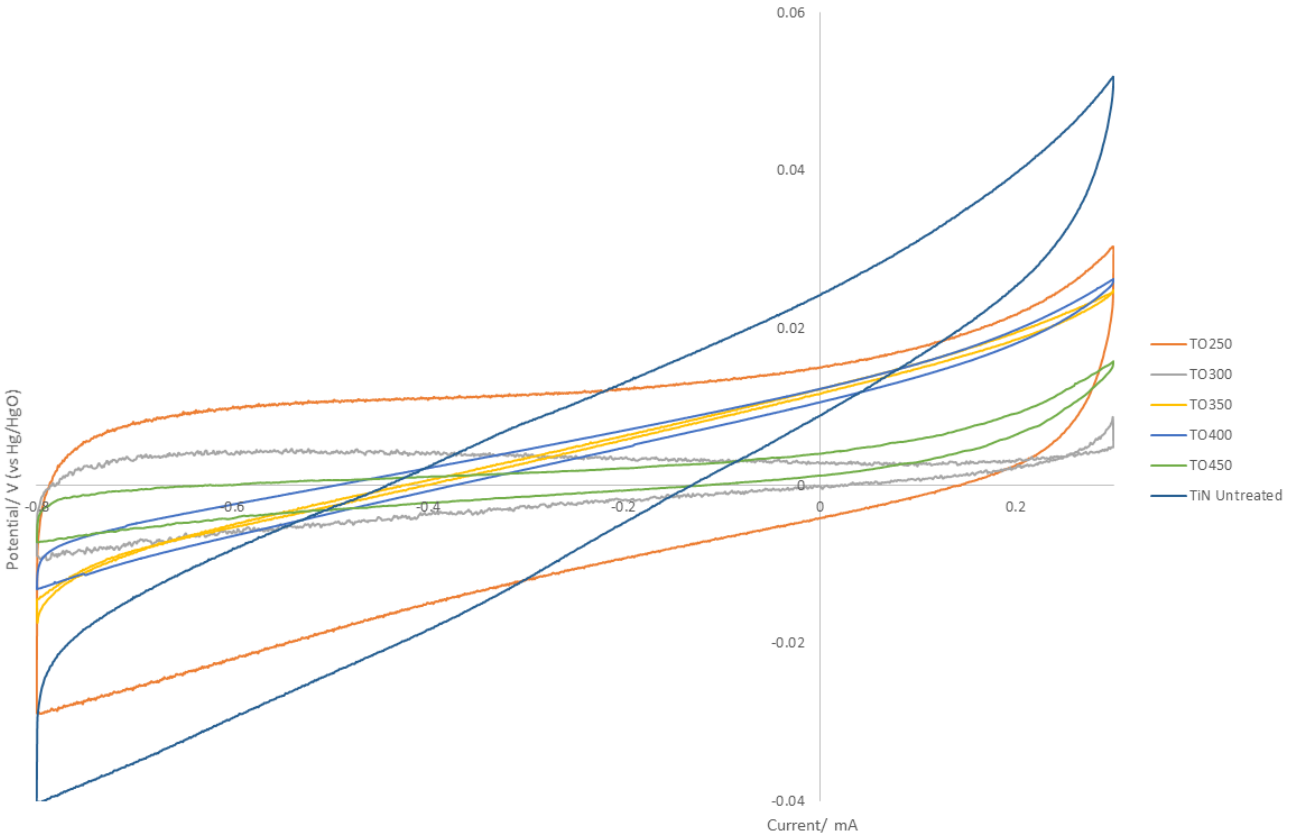

Fig. S6 The 5th CV cycle at 10 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

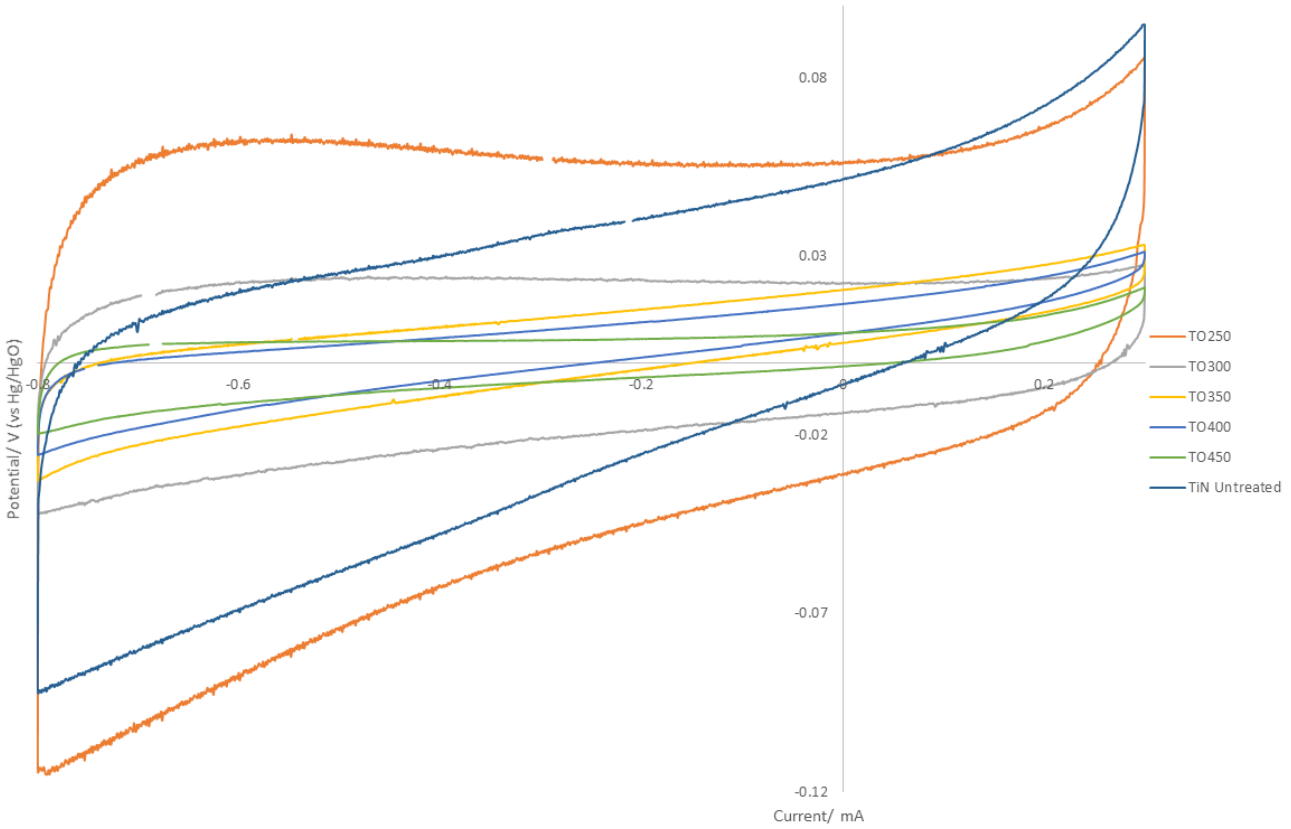

Fig. S7 The 5th CV cycle at 50 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

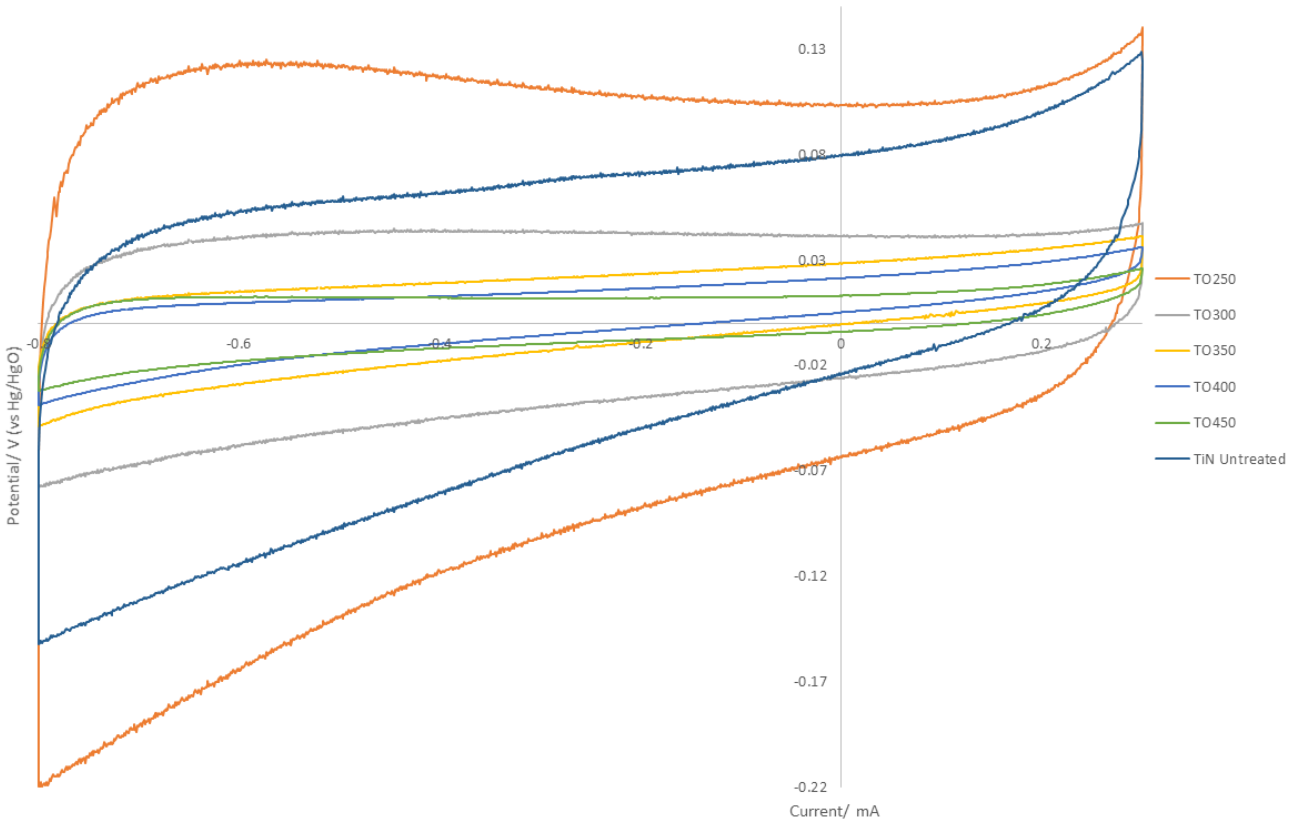

Fig. S8 The 5th CV cycle at 100 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

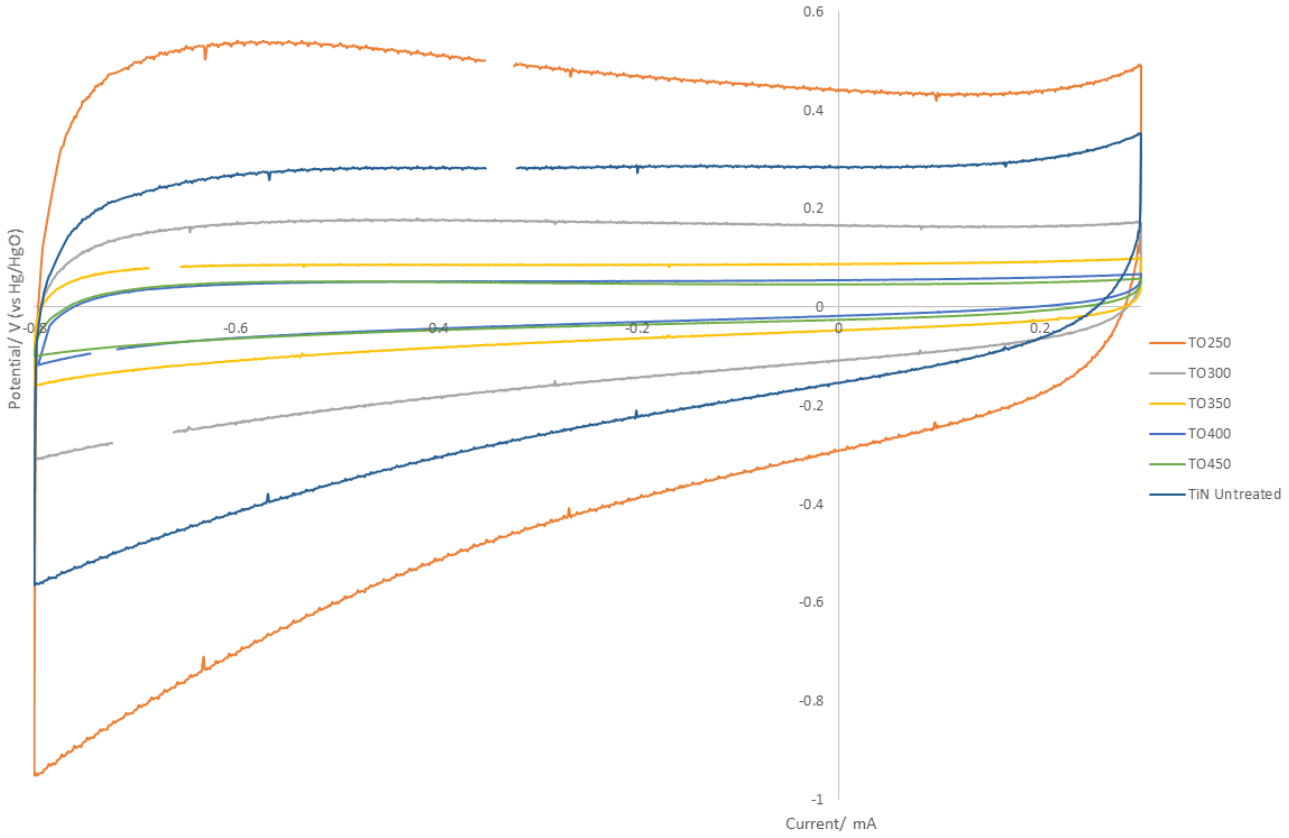

Fig. S9 The 5th CV cycle at 500 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

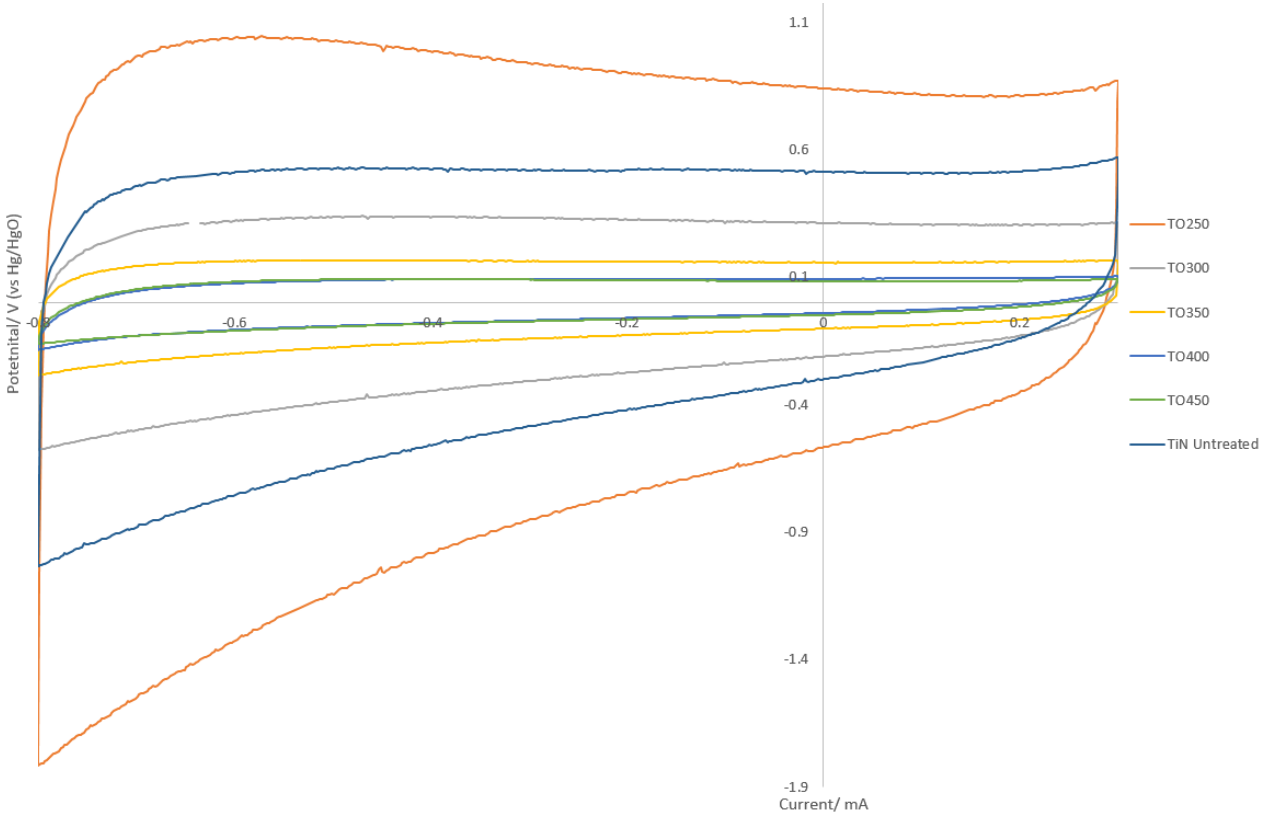

Fig. S10 The 50th CV cycle at 1000 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and thermally oxidized (24 h at temperatures as labelled, e.g. TO300 = 300 °C) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

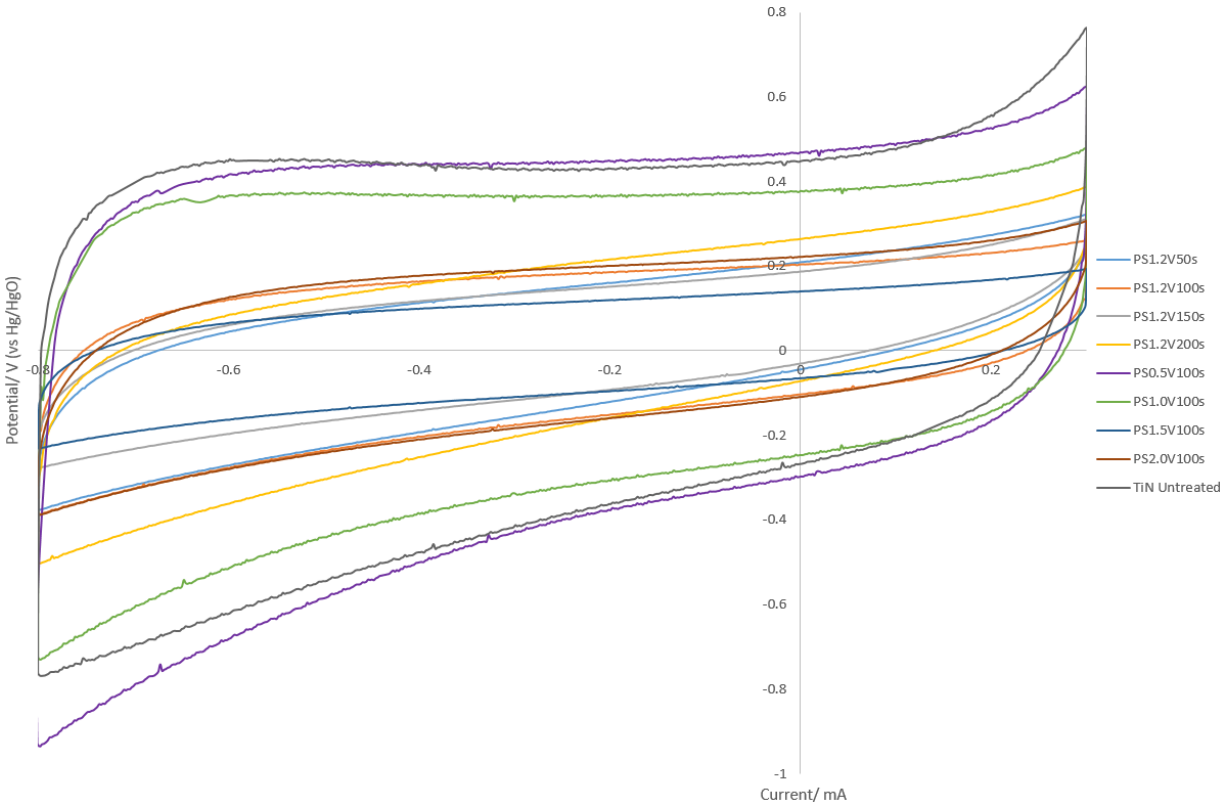

Fig. S11 The 5th CV cycle at 1000 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

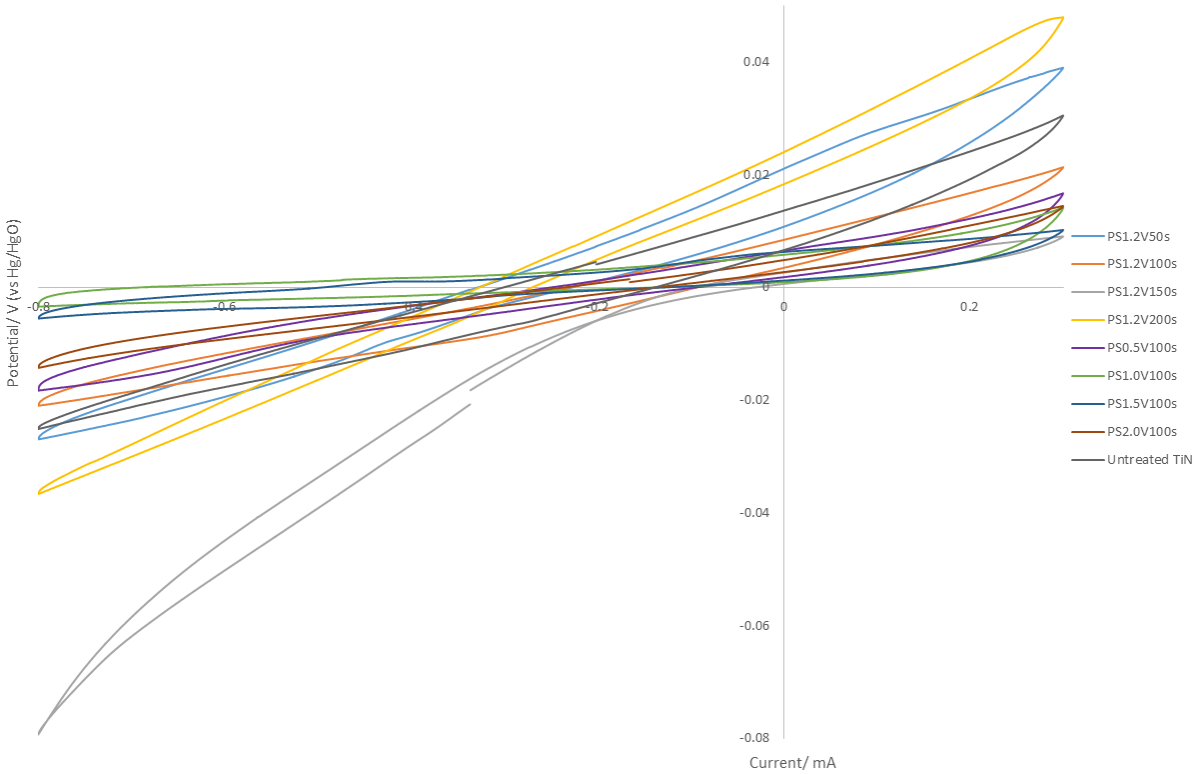

Fig. S12 The 5th CV cycle at 1 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

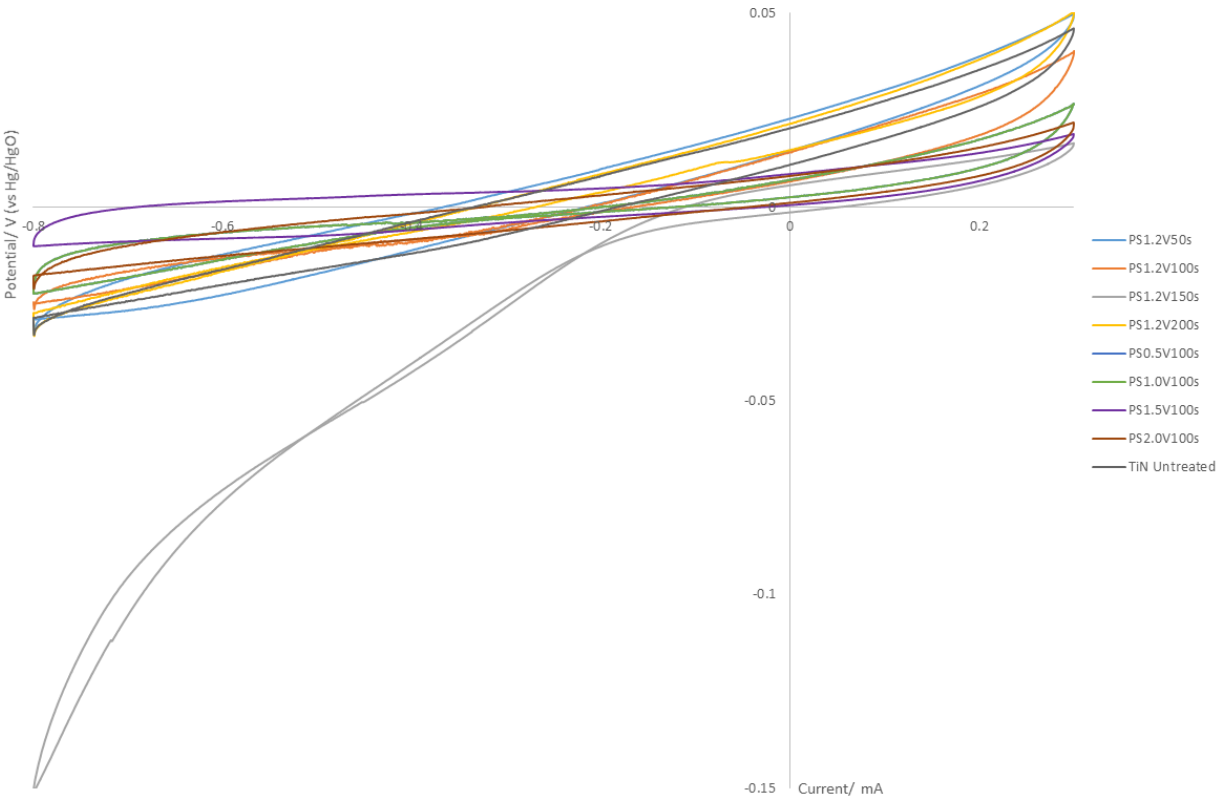

Fig. S13 The 5th CV cycle at 5 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

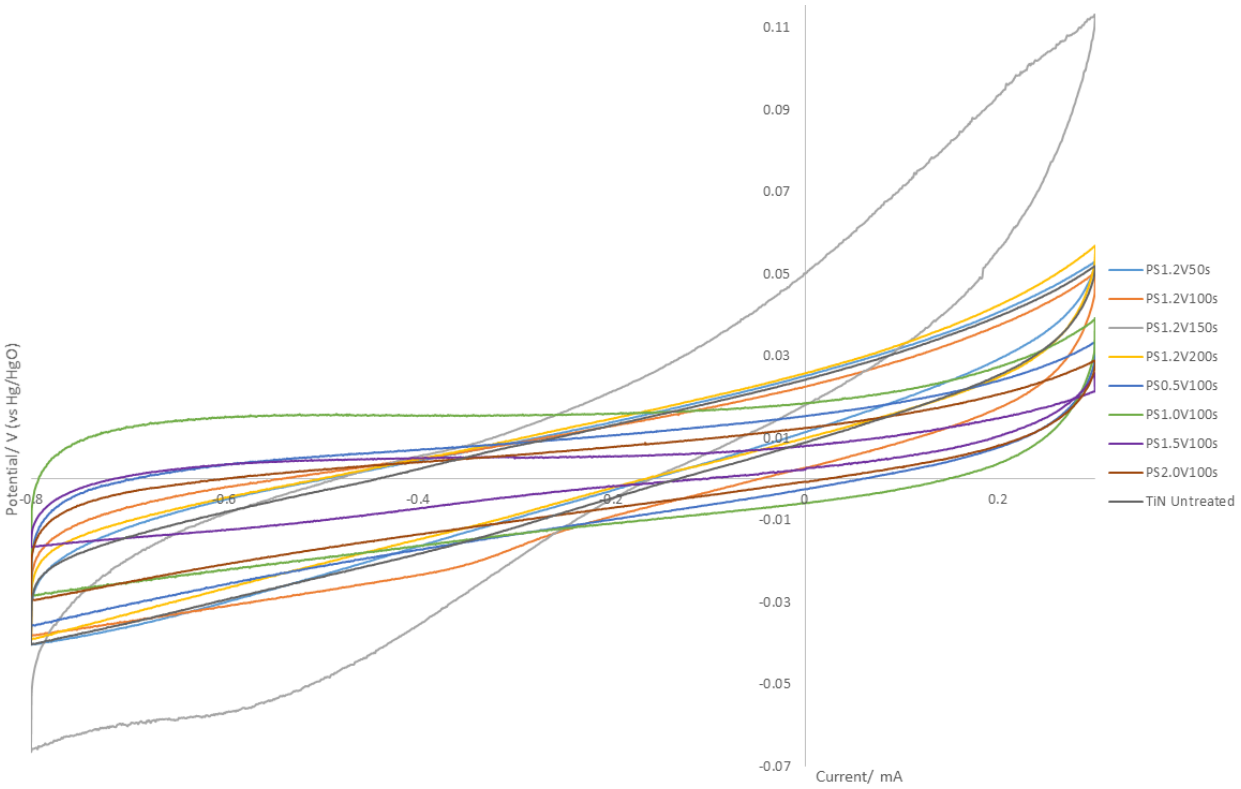

Fig. S14 The 5th CV cycle at 10 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

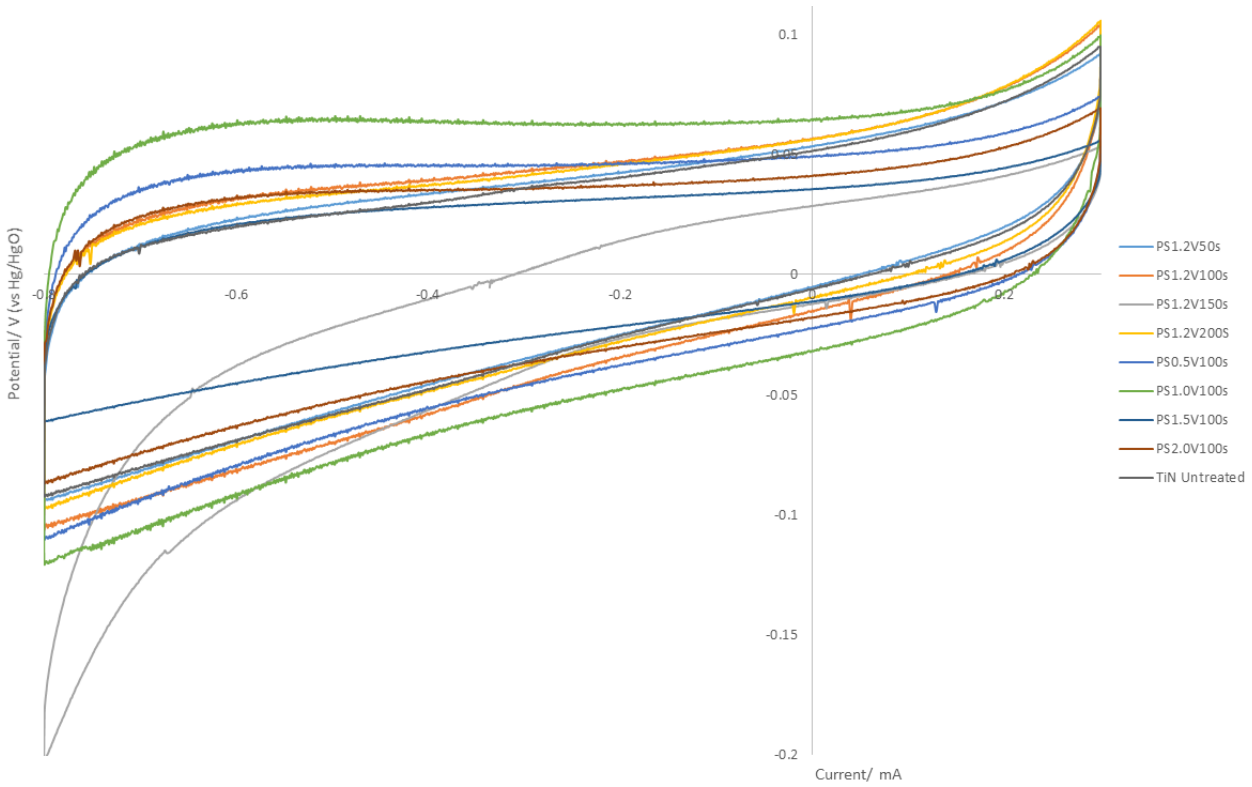

Fig. S15 The 5th CV cycle at 50 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} KOH$_{(aq)}$.

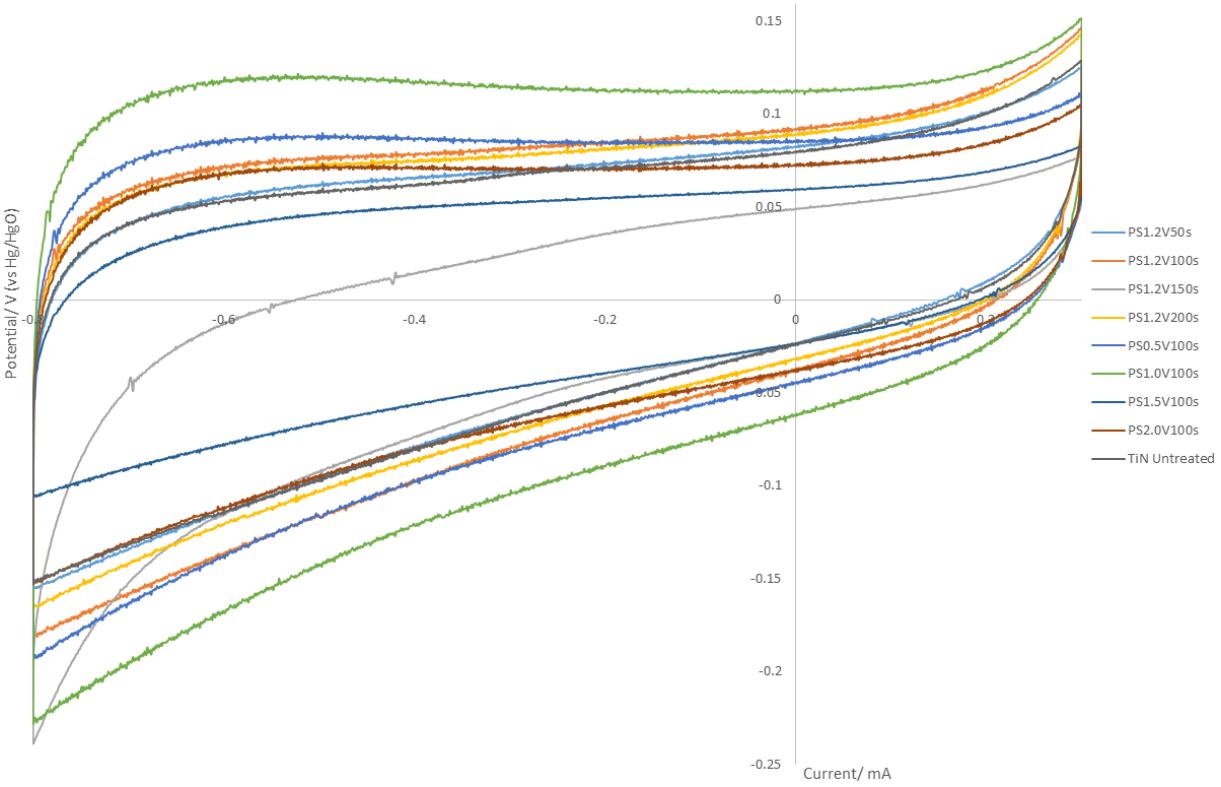

Fig. S16 The 5th CV cycle at 100 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} KOH$_{(aq)}$.

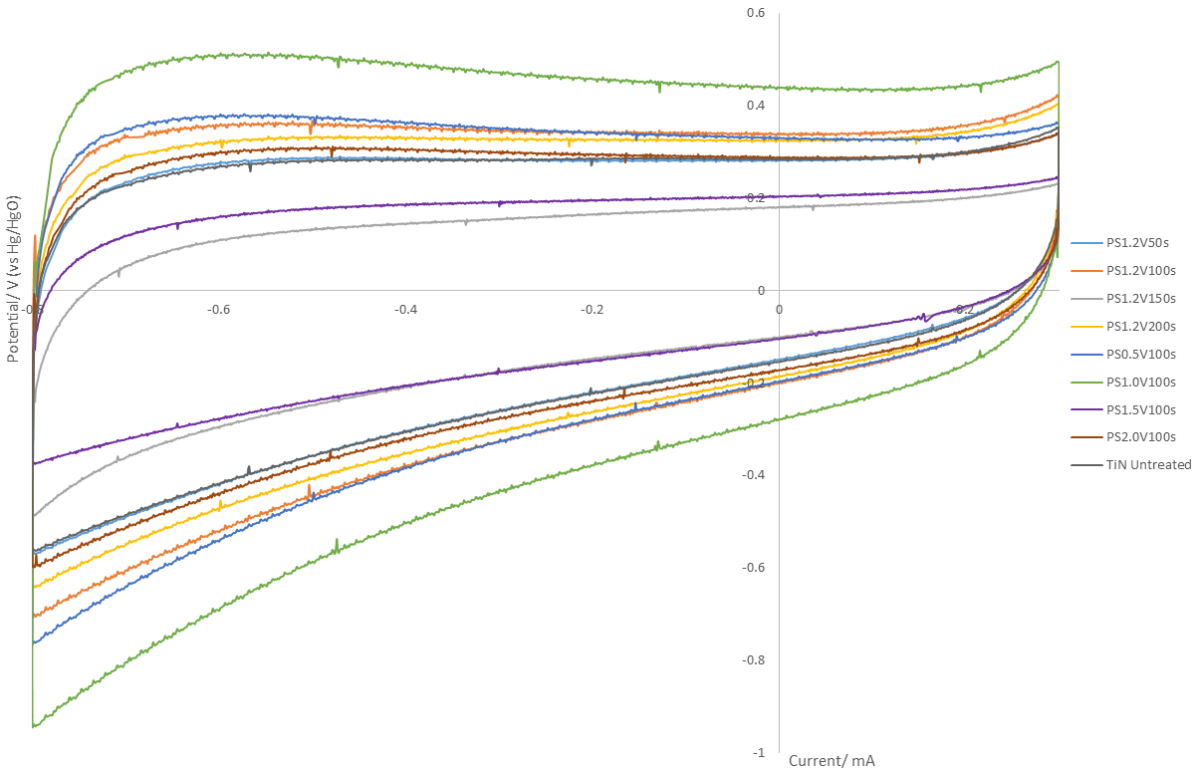

Fig. S17 The 5th CV cycle at 500 mV s^{-1} (potentials *vs* Hg/HgO) of as-prepared and potential step oxidized (potential and duration as labelled, e.g. PS1.2V50s was held at +1.2 V vs Hg/HgO for 50 s) TiN foils in 6 mol dm^{-3} $KOH_{(aq)}$.

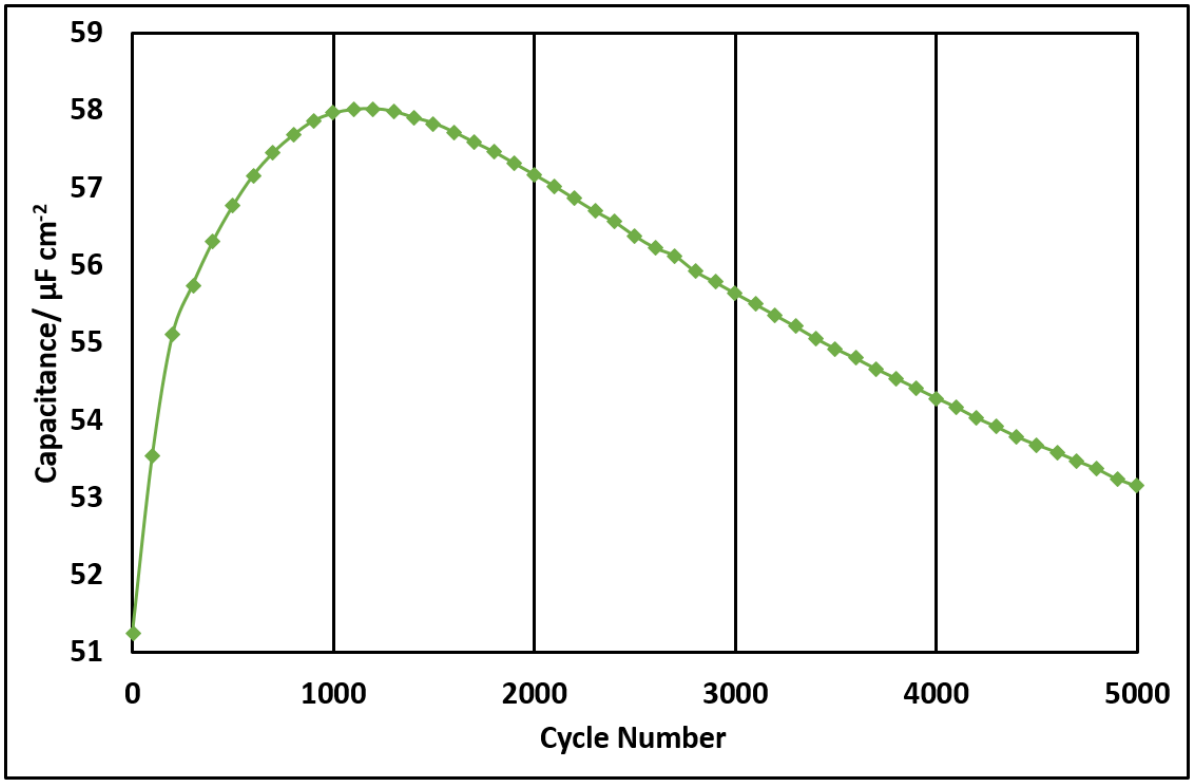

Fig. S18 Areal capacitance of a TiN electrode subjected to potential step oxidation at 1.0 V vs Hg/HgO for 100 s before applying CV scans as shown in Fig. 5. The figure shows the capacitance variation during 5000 final scans at 1000 mV s^{-1}.

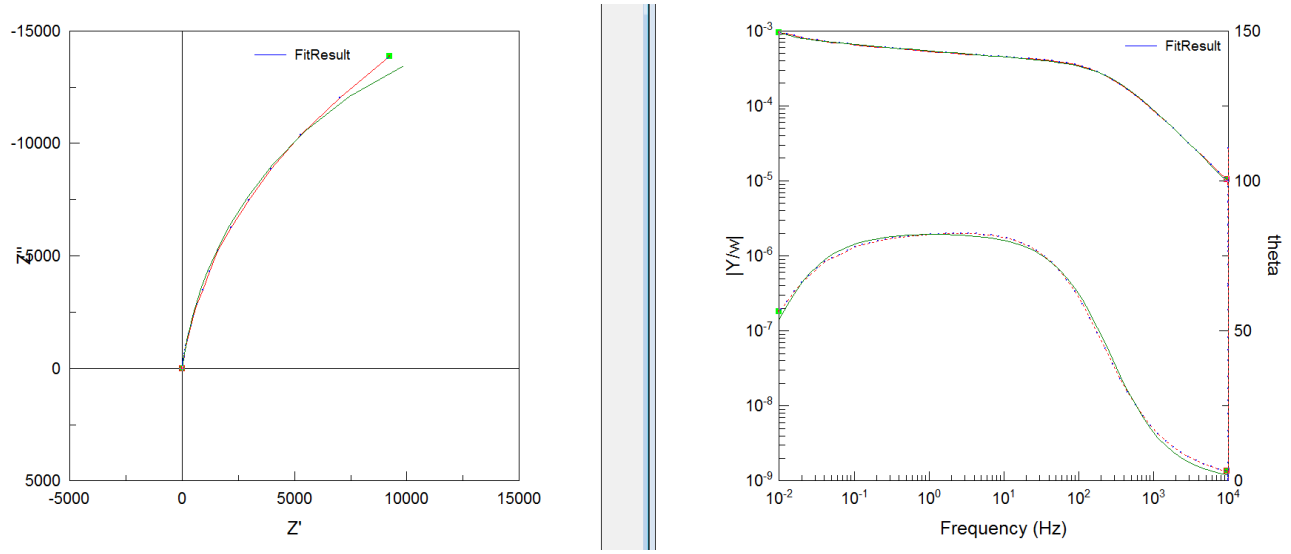

Fig. S19 ZView fits to the Nyquist (left) and capacitance/phase angle (right) plots of an untreated TiN electrode collected at the open circuit potential (~-0.4 V) after CV and galvanostatic cycling.

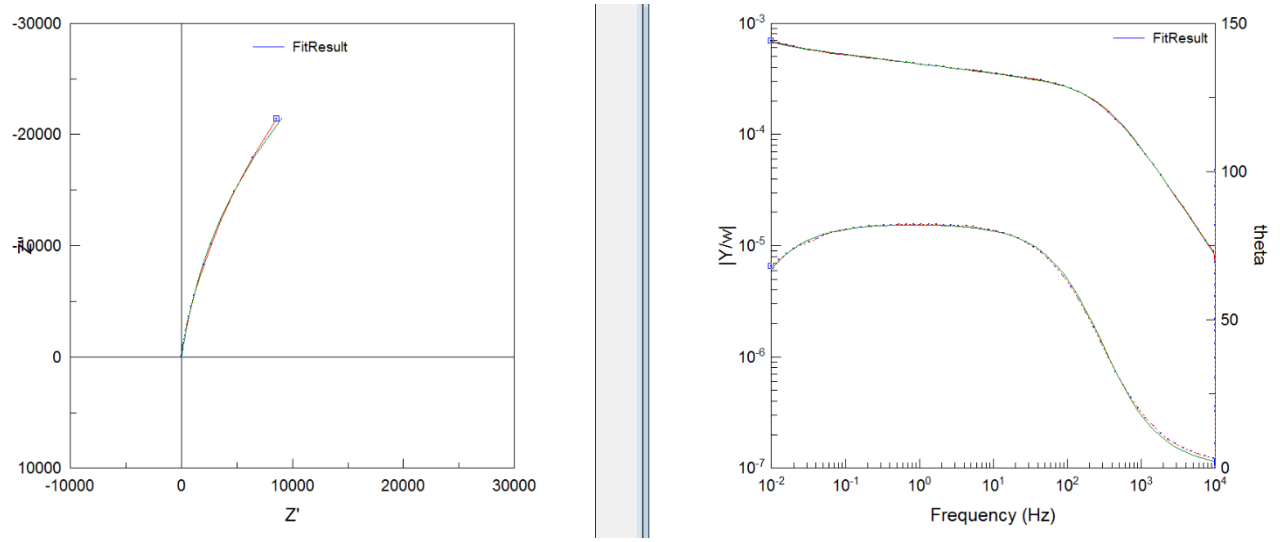

Fig. S20 ZView fits to the Nyquist (left) and capacitance/phase angle (right) plots of a potential step oxidized (1.2 V 150 s) TiN electrode collected at the open circuit potential (~-0.4 V) after CV and galvanostatic cycling.

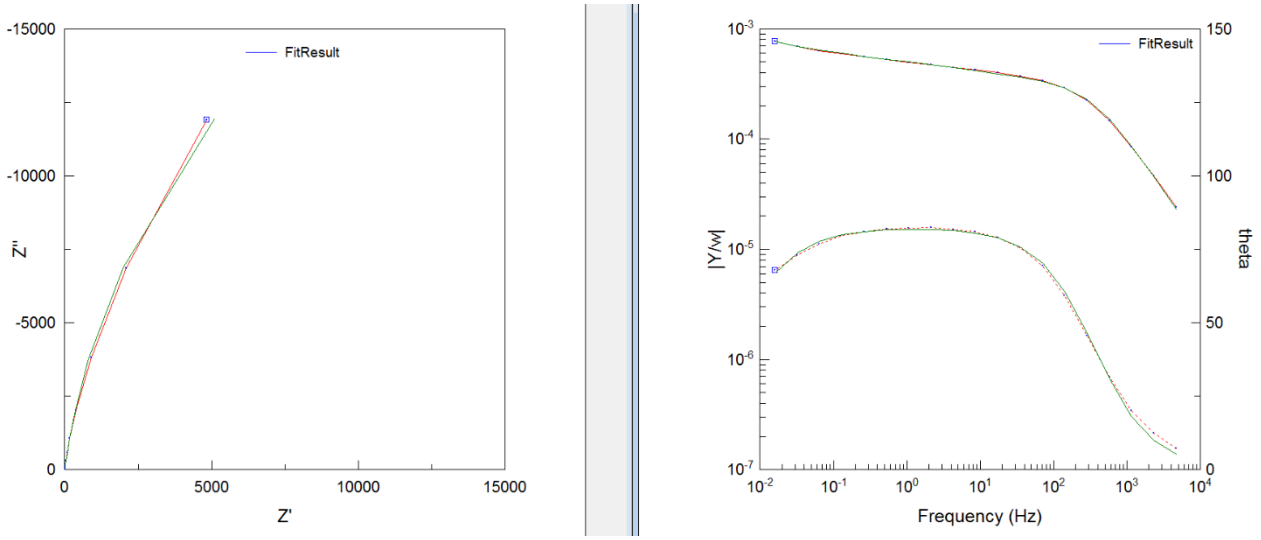

Fig. S21 ZView fits to the Nyquist (left) and capacitance/phase angle (right) plots of a potential step oxidized (1.0 V 100 s) TiN electrode collected at the open circuit potential (~-0.4 V) after CV and galvanostatic cycling.

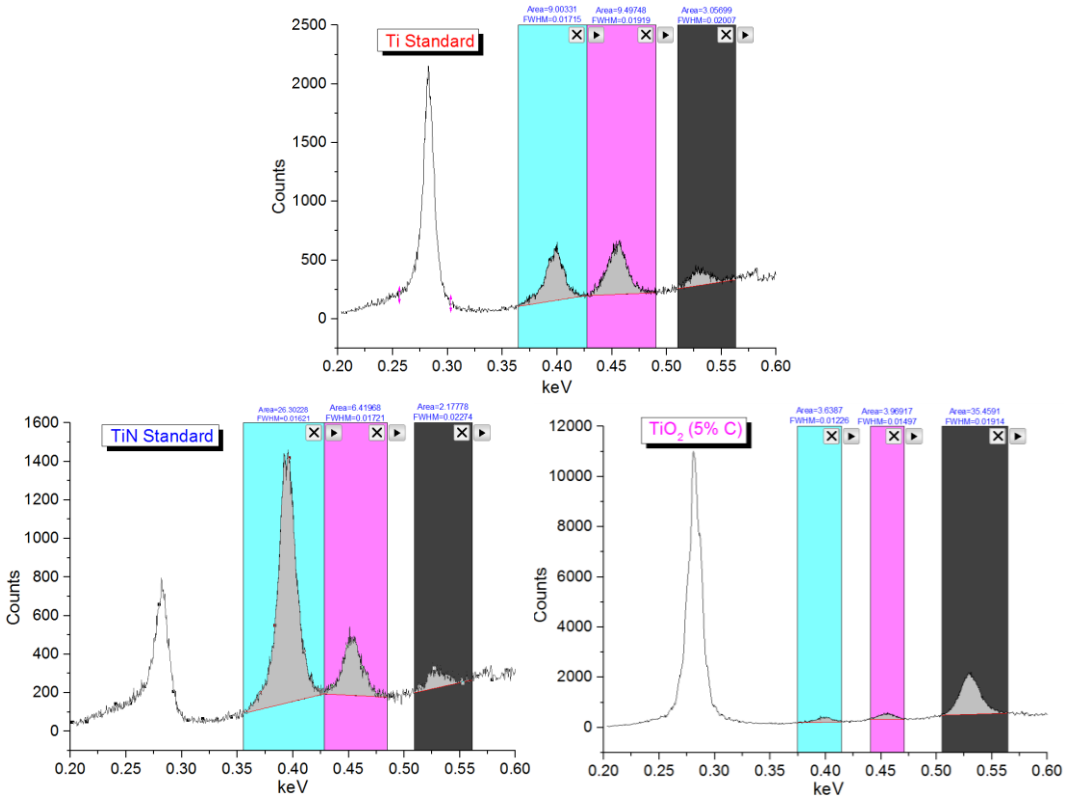

Fig. S22 WDX spectra of titanium (top), titanium nitride (bottom left) and titanium dioxide (bottom right) standards used in analysis of the WDX spectra of the potential step oxidized samples.

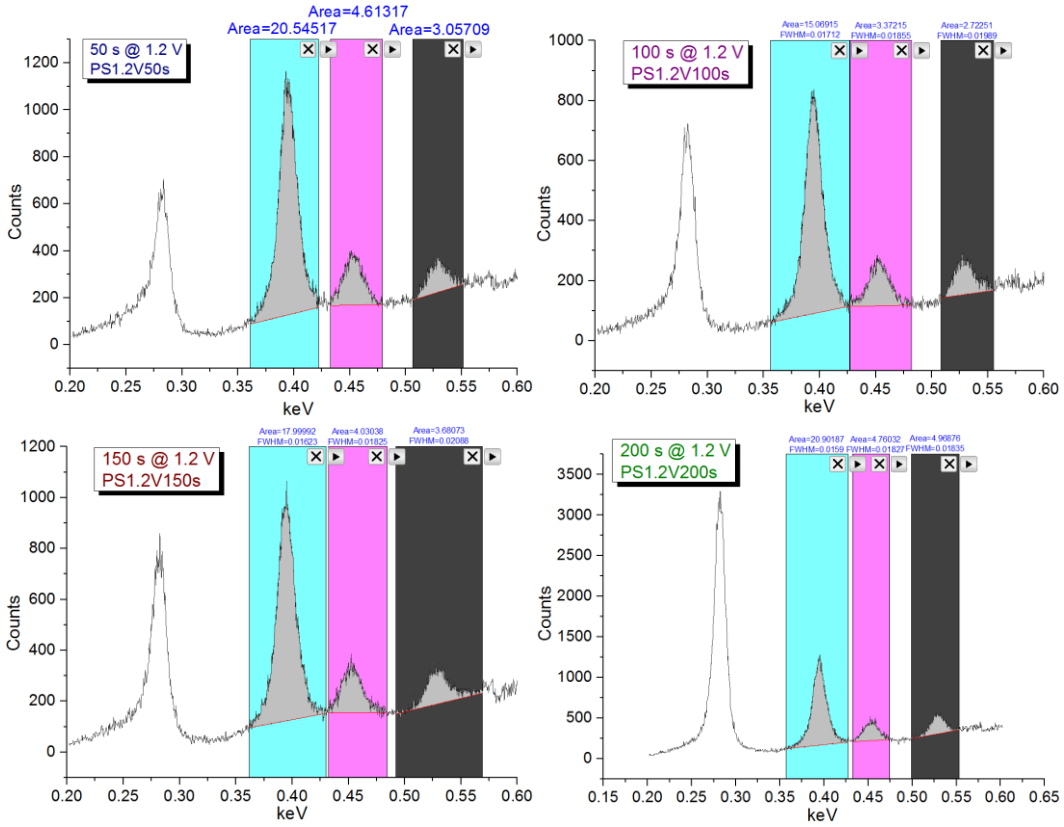

Fig. S23 WDX spectra of titanium nitride foils after potential step oxidation at 1.2 V for 50 (top left), 100 (top right), 150 (bottom left) or 200 s (bottom right).

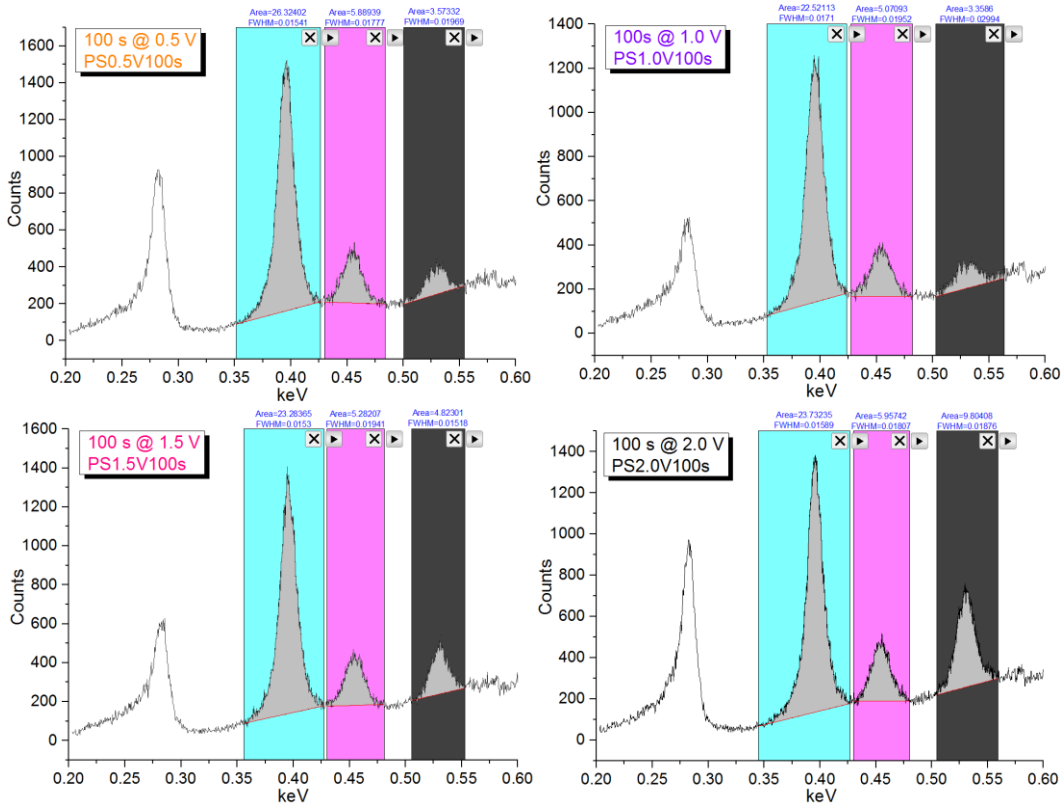

Fig. S24 WDX spectra of titanium nitride foils after potential step oxidation at 0.5 (top left), 1.0 (top right), 1.5 (bottom left) or 2.0 V (bottom right) for 100 s.

Table S2 Ratio of elements produced after each potential step method and the resulting oxygen and nitrogen content

	0.39 eV (Ti+N)	**0.45 eV (Ti)**	**0.53 eV (O)**					
Ti	6.17	8.57	2.71	Ti+N/Ti	0.719953			
TiN	23.67	5.54	1.62	Ti+N/Ti	4.272563			
TiO2	2.43	3.39	29.45	O/Ti	8.687316			
				Ti+N/Ti	**O/Ti**		**N:Ti**	**O:Ti**
PSO 1.2 V 50 s	18.51	4.15	2.19	4.460241	0.527711		1.255483	0.12149
PSO 1.2 V 100 s	13.6	2.8	2.24	4.857143	0.8		1.367204	0.184177
PSO 1.2 V 150 s	15.98	2.56	2.44	6.242188	0.953125		1.757071	0.219429
PSO 1.2 V 200 s	18.63	4.15	5.27	4.489157	1.26988		1.263622	0.292353
PSO 0.5 V 100 s	21.27	4.25	2.33	5.004706	0.548235		1.408741	0.126215
PSO 1.0 V 100 s	21.67	3.51	2.48	6.173789	0.706553		1.737818	0.162663
PSO 1.5 V 100 s	22.93	3.82	4.18	6.002618	1.094241		1.689636	0.251917
PSO 2.0 V 100 s	22	4.92	7.41	4.471545	1.506098		1.258665	0.346735

In analysis of the PSO samples:

- "Ti+N / Ti" taken to scale linearly from 0.72 at $TiN_{0.0}$ to 4.27 at $TiN_{1.0}$
- O/Ti scaled relative to a value of 8.69 for $TiO_{2.0}$

References

1 *Inorg. Cryst. Struct. Database (ICSD, Fiz Karlsruhe) accessed via EPSRC-funded Natl. Chem. Database Serv. hosted by R. Soc. Chem.*

2 *PDF-2 (Powder Diffr. File), 2012 release, Int. Cent. Diffr. Data, Swart. PA.*