

Ultra fast electrochromic switching of nanoporous tungsten-tantalum oxide films

Electronic supplementary information (ESI) †

1. Preparation and anodization of the W-Ta alloy

The home-made single phase W-Ta alloy was prepared by mixing tungsten and tantalum wires in an at% ratio of 80/20. The raw material was fused by vacuum arc melting. The as received ingots were ground and polished to mirror finish. The grain size distribution of the W-Ta alloy is shown in Fig. 1Sa, the grains exhibit a size from 50 to 500 μm . The most occurring grain size is in the range of 150 to 300 μm . A mechano-chemical polishing treatment in a mixture of H_2O_2 and a non-crystallizing colloidal silica suspension results in the grain microstructure, shown in Fig. 1Sb.

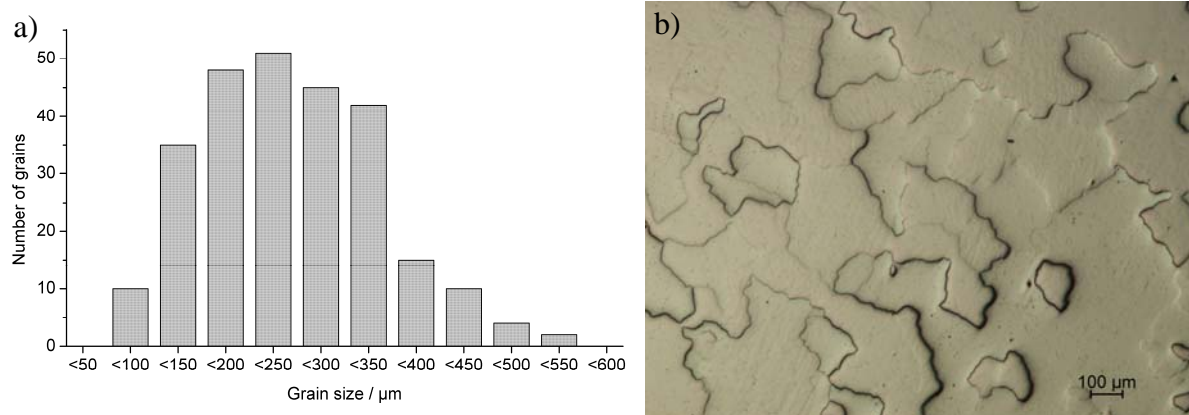


Fig. S1a) grain size distribution of the W-Ta alloy b) light microscopy picture of the mechano-chemical-polished W-Ta alloy surface

The anodization treatment was carried out using an electrochemical o-ring cell with a conventional three electrode configuration with the sample being the working electrode, a platinum counter electrode and a Pt wire serving as a pseudo reference electrode. The nanoporous oxide layers are formed in ethylene glycol electrolyte containing a small amount of hydrofluoric acid. Compared to other valve metals the pore diameter of the grown morphology did not significantly change with the applied potential and the as grown porous layer thickness is limited to approximately 100 nm.

2. Anodization on pure tungsten

The anodization of pure W was realized in 1 M H_2SO_4 solution with addition of 0.5 wt% NaF for 30 min at 40 V. Fig. 2Sa shows the SEM top view and Fig. 2Sb the cross sectional image of a reference porous oxide layer grown on pure W, with a typical pore size of approximately 100 nm and a thickness of the WO_3 layer of approximately 200 nm.

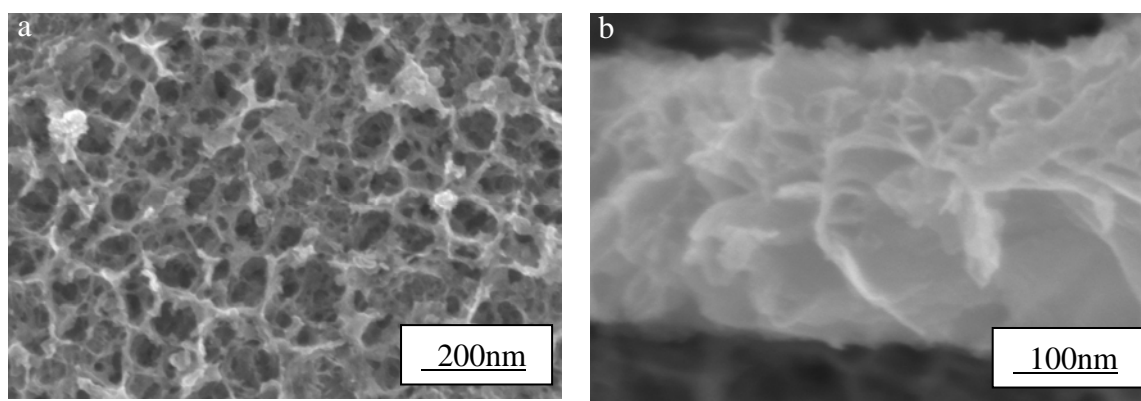


Fig. S2a) SEM top and cross sectional (b) view of the porous anodic oxide layers on W grown in 1M H₂SO₄ + 0.5wt% NaF for 1h at 40V.

3. Optimization of the anodization conditions

Some of the different electrolytes explored for anodization and the resulting oxide morphologies on the W-Ta alloy are shown in Fig S3a) - i). In 17.5 M H₃PO₄ + 0.5 M HF (Fig. S3a) a completely smooth oxide morphology without any nanostructure is obtained. Anodization in 0.3 M oxalic acid + 0.2 M NH₄F (Fig. S3b) produces a rough and etched oxide surface. In glycerol + 0.2 M NH₄F (Fig. S3c) a network of pores with random pore sizes is formed. In 14.8 M H₂SO₄ + 0.8 M HF (Fig. S3d) a thin and smooth dimpled oxide layer is obtained. In ethylene glycol + 0.2 M HF (Fig. S3e) self-ordered homogenous pores on the oxide surface are formed. In glycerol + 1 M HF (Fig. S3f) an inhomogeneous thin oxide layer with selectively grown dimples is formed. In 1 M H₂SO₄ + 0.5 wt% NaF (Fig. S3g) a roughly etched oxide morphology is obtained. In 1 M (NH₄)₂SO₄ + 0.2 M NH₄F (Fig. S3h) a inhomogeneous surface is visible with some grains showing an oxide layer and some not. In ETG + 0.2 M NH₄F + 15 vol% H₂O (Fig. S3i) an oxide layer with partially homogeneous areas is formed. The most suitable and reliable oxide morphology was grown in an ETG + HF electrolyte (Fig. S3e). The formed pores are homogeneously distributed all over the anodized surface area and could be produced with a high reproducibility. Further anodization parameters, such as voltage, fluoride concentration, sweep rate and anodization time were investigated for this specific electrolyte. Under optimized conditions the pores have a diameter of approximately 10 nm.

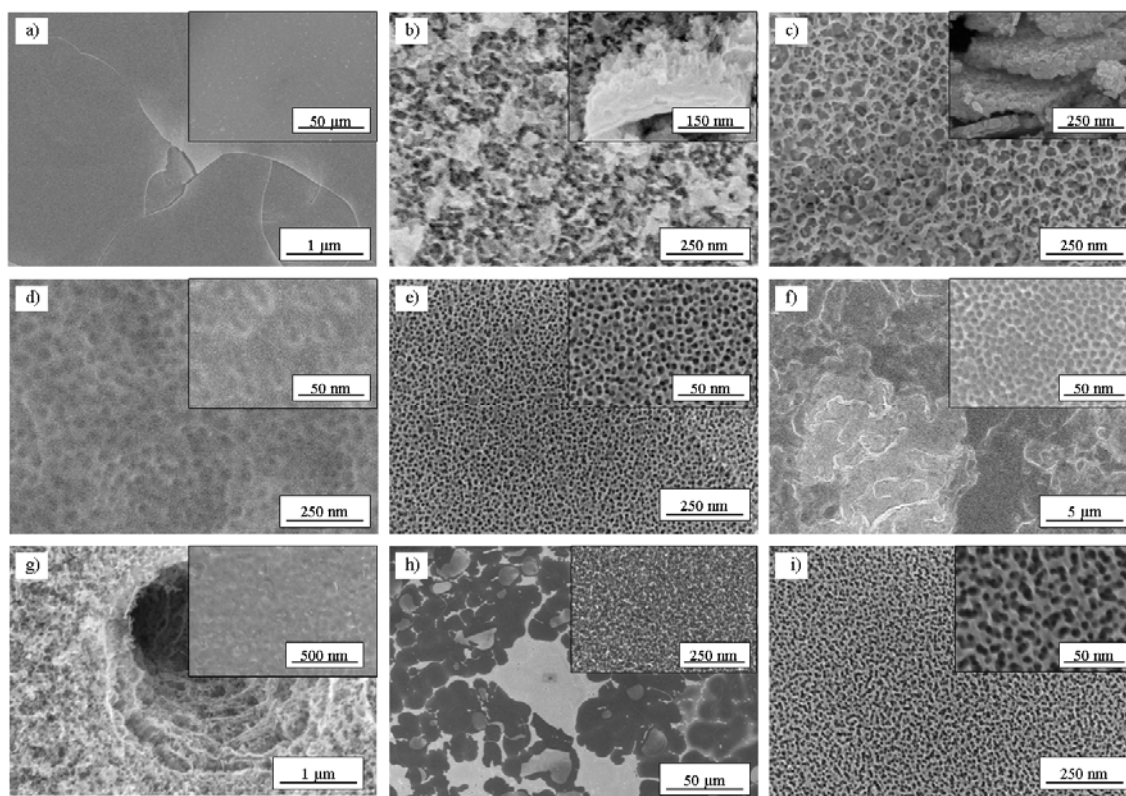


Fig. S3 SEM images of the oxide morphologies obtained in different electrolytes a) the electrolyte of 17.5 M H_3PO_4 + 0.5 M HF b) 0.3 M oxalic acid + 0.2 M NH_4F c) glycerin + 0.2 M NH_4F d) 14.8 M H_2SO_4 + 0.8 M HF e) ETG + 0.2 M HF f) glycerin + 1 M HF g) 1 M H_2SO_4 + 0.5 wt% NaF h) 1 M $(\text{NH}_4)_2\text{SO}_4$ + 0.2 M NH_4F i) ETG + 0.2 M NH_4F + 15 vol% H_2O

The pore size as well as the interpore spacing show no direct dependency on the applied potential. However, the thickness of the as grown anodic layers is limited to approximately 100 nm and shows a dependency on the applied potential as well as on the anodization time. The influence of the anodization time on the layer thickness is shown in Fig. S4a). The thicknesses of the porous layers were revealed from sputter depth profiles. A typical XPS sputter-depth profile of the porous anodic oxide layer is shown in Fig. S4b).

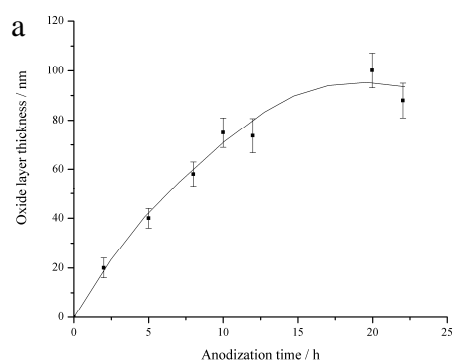


Fig. S4 a) dependency of the oxide layer thickness on the anodization time for W-Ta alloy anodized in ethylene glycol + HF at 10 V (sweep rate 0.05 V/s).

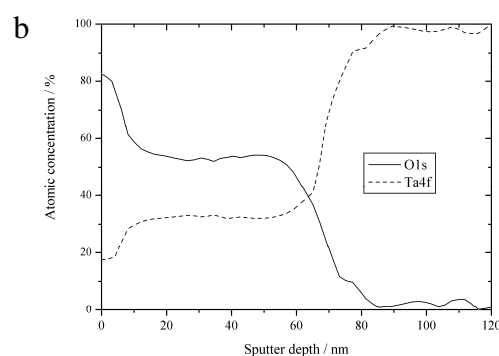


Fig. S4 b) XPS sputter-depth profile of tantalum (Ta4f) and oxygen (O1s). The porous oxide layer grown on W-Ta alloy anodized in stirred ethylene glycol + HF for 10 h at 10 V (sweep rate 0.05 V/s).

Due to the observed thickness limitation in Fig. S2 a) it can be assumed that under the present conditions no continuous oxide growth can be maintained. It should be noted that in order to

grow reproducible layers, a sufficient fluoride concentration as well as continuous stirring of the electrolyte is needed. The layers with the best homogeneity were formed in stirred ethylene glycol electrolyte with 0.2 M HF at an applied potential of 10 V (sweep rate 0.05 V/s) within 10 h.

4. XPS and XRD

The composition of the porous anodic oxide layers on the W-Ta alloy was investigated by X-ray photoelectron spectroscopy (XPS Physical Electronics 5600). The respective XPS results are shown in Fig. S5 a and b. The spectra show four characteristic peaks. The first two peaks at 26.5 eV and 28.3 eV can be attributed to $4f_{7/2}$ and $4f_{5/2}$ of Ta^{5+} ; the second two peaks are assigned to $4f_{7/2}$ and $4f_{5/2}$ W^{6+} at 35.8 eV and 37.9 eV. The peaks of W^{5+} , W^{4+} , W^0 at 33.0 eV, 31.9 eV, 30.5 eV and 35.1 eV, 34.0 eV, 32.69 eV show no significant peak. The oxygen peak O1s was detected at 530.2-532.1 eV with a shoulder at higher energies of 532.1-533.1 eV. The peak at 531 eV can be assigned to the O^{2-} oxygen and the shoulder at 533 eV belongs to OH^- oxygen. The XPS analysis revealed a layer composition of approximately 36 at% W^{6+} , 10 at% Ta^{5+} , together with 40 at% O^{2-} and 14 at% OH^- . A similar composition was confirmed by EDX analysis. A structural XRD analysis was performed in order to further explore the porous oxide layers. The corresponding XRD patterns are shown in Fig. S5c. The bare W-Ta alloy, the as grown anodic oxide layer and the annealed anodic oxide layers are compared to the anodized and annealed WO_3 layers on pure W. Distinct peaks can be localized at 40.3° , 58.3° and 73.2° , which can be attributed to the W metal from the substrate. The spectra of the as grown layers, as well as the spectrum of the annealed layers show no additional peaks compared to the bare W-Ta substrate. The annealed oxide layer shows in both cases the highest intensity. Thus, the annealing treatment of the mixed and WO_3 oxide layers for 1 h at $300^\circ C$ does not result in the formation of crystalline layers. According to the performed analysis the amorphous porous oxide layers of the W-Ta alloy consist of a mixed amorphous oxide.

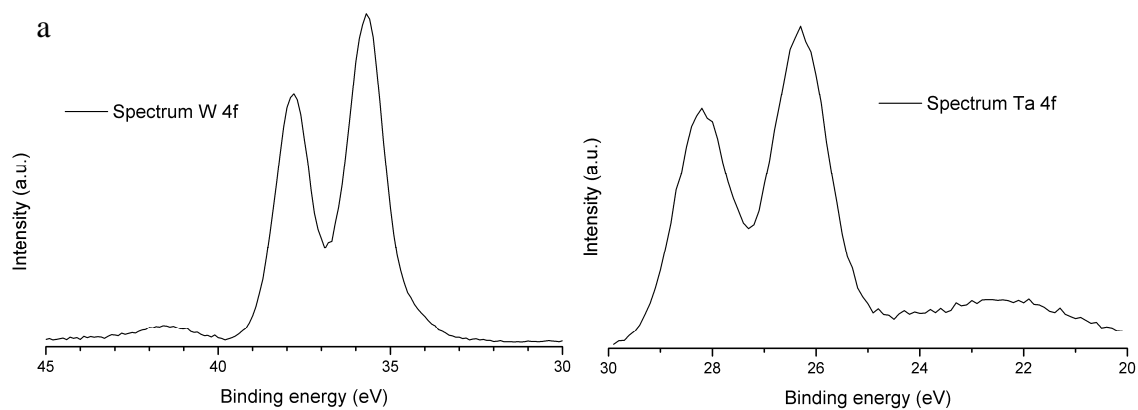


Fig S5 a) XPS- spectrum of the formed oxide layer on W-Ta alloy, showing the W4f and Ta4f peaks

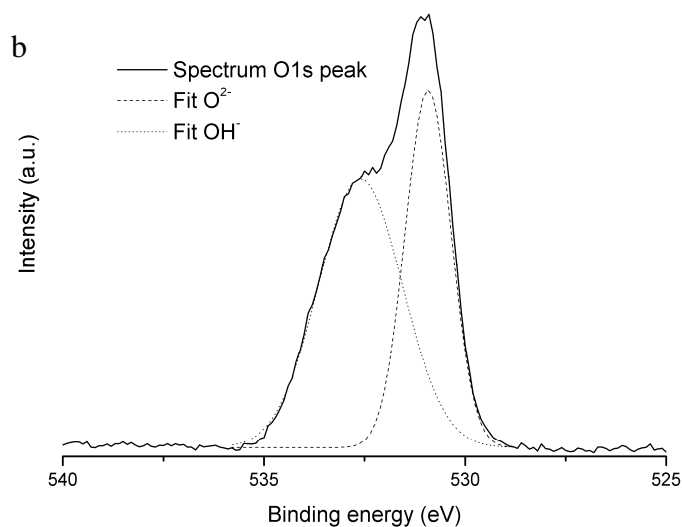


Fig. S5 b) XPS-Pattern of the O 1s Peak

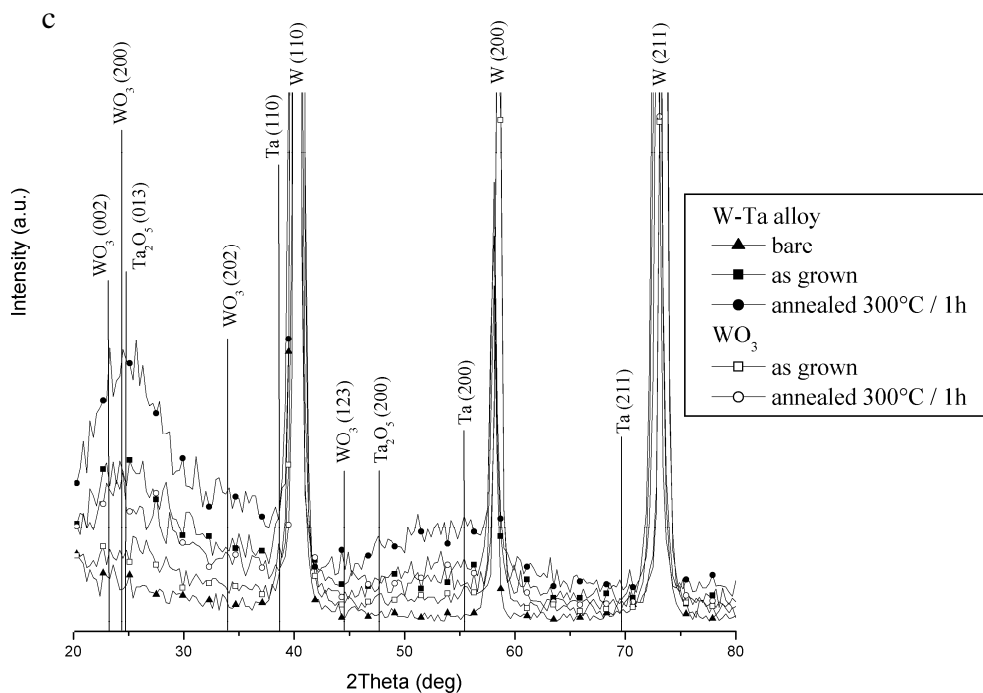


Fig. S5 c) XRD- spectra of W-Ta and WO₃ for the bare, as grown and annealed anodic oxides by using a thin-film XRD instrument.

4. Electrochromic Measurements

The electrochromic measurements were carried out in 0.1 M H₂SO₄ with a conventional three electrode setup. The sample was contacted with a copper block and attached to a bottom O-ring cell. The counter electrode used was a platinum sheet and a Ag/AgCl electrode served as reference electrode. The optical in situ measurements were carried out using a fiber optic illuminator at 620 nm (tungsten halogen lamp, Ocean Optics). For the voltammograms and chronoamperometric measurements an Autolab PGSTAT 30 Potentiostat/Galvanostat was used. The CVs recorded after 50 cycles and 100 cycles show a slightly changing characteristic for the porous WO₃, presumably caused by the dissolution of WO₃. Fig. S6a shows the cyclic voltammograms (CVs) in 0.1 M H₂SO₄ for the grown nanostructured oxide layers on W and the W-Ta alloy. The CVs were carried out between -0.5 V and 1 V with a scan rate of 50 mV/s for 100 cycles. In comparison to pure WO₃, the grown oxide on the W-Ta alloy shows much lower current density at a comparable layer thickness. For the oxide grown on the W-Ta alloy absolutely identical CVs even after 100 cycles are obtained, indicating a high stability of these presented nanostructures. The charge transfer characteristics of the porous oxide layers were obtained by step transient measurements. The exchanged charge in a 30 sec switching step during cathodic (Q_c) and anodic (Q_a) reactions is for the oxide layer on the W-Ta alloy Q_c: -2.03 mC/cm² and Q_a: 0.65 mC/cm², respectively. For the porous WO₃ layer a Q_c of -2.96 mC/cm² and a Q_a of 3.68 mC/cm² is measured. The WO₃ layer exhibits a higher charge transfer rate. The reversibility reaction of the intercalation can be estimated from the ratio of the charge densities (Q_a/Q_c). The porous layer on the W-Ta alloy and the porous WO₃ layers showed reversibility ratios of 0.32 and 0.8, respectively. Interesting, however, is that in the case of the mixed porous oxide layer almost two-thirds of the initially inserted charge remain in the layer. In other words, only one third of the inserted charge is extracted sufficient for complete switching to the transparent (bleached) state.

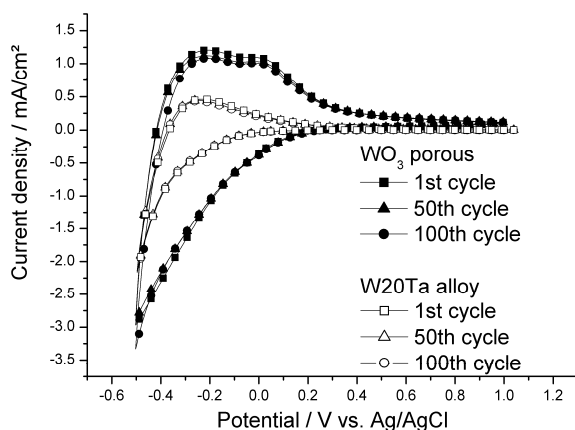


Fig S6 (a) Cyclic voltammogram of porous WO₃ and porous W-Ta oxide layers in 0.1 M H₂SO₄ with the potential scanned from -0.5 V to 1.0 V using a scan rate of 50 mV/s

5. Movies

The attached movies “1 tungsten 10 s cycling” and “2 W-Ta alloy 1 s cycling” show the electrochromic measurements of the grown oxide on tungsten and on the W-Ta alloy in 0.1 M H₂SO₄. The applied potential in cathodic direction is -0.5 V and in anodic direction +1 V. The movie for tungsten shows a 10 s step and the movie for the W-Ta alloy a 1 s step cycling. The grown oxides on tungsten turn into a dark blue when the cathodic potential is applied. The switch to anodic potential after 10 s shows no significant change in coloration. The tungsten oxide layer stays dark blue. In contrast the grown oxide layer on the W-Ta alloy shows a fast switching behavior between the colored and bleached state.