Library suggestions for TiO_2 skin OER catalysts

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Based on the conditions that four oxides can be combined and that one has to be TiO_X, we propose two different materials libraries.

- (I) The first library aims at making solid solution rutile oxides, where the metal ions are primarily in 4+ oxidation state and where the Fermi-level can be manipulated to give the predicted catalytic optimum.
- (II) The second library aims at making ordered mixed valence rutile oxides, where a high number of interesting structures are situated at the binary metal oxide edge.

We further suggest that, to promote a surface TiO_2 skin/layer, the libraries are heated in O_2 to drive TiO_2 to the surface and/or the libraries are rotated and exposed to additional TiO_X (post creation).

(I) Solid solution rutile oxides.

Based on the Fermi levels of the pure rutile oxides (Fig. 1) we suggest to try the composition **Mn-Mo-Pt-Ti**. As can be seen from the diagram Mo and Pt have slightly higher values than the ideal (ca. 18.5 eV relative to the O2s state), while Ti and Mn have lower values, and a mixture should therefore have approximately the right value. We have performed calculations for Mn4Pt14Mo3Ti3 with 1 TiO_2 layer (predicted E_F=18.5eV) on top and as can be seen from Fig. 2 the activity is close to the top of the volcano. Calculations for the equimolar composition are in progress (predicted E_F 18.3eV).

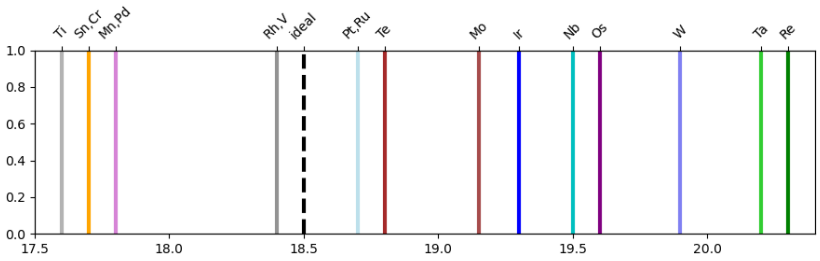

Fig. 1. Calculated Fermi levels relative to the O2s peak for the pure rutile oxides.

In addition to the expected activity we note that Pt, Mn and Ti are all stable in the rutile (Mn, Ti) or rutile-like (Pt) structure at pH = 0 and U=1.6V. The oxides of Pt, Mn and Mo have no band gap in DFT

calculations and we therefore also expect a good conductivity. The main downside is the price and scarcity of Pt, but hopefully we don't need a large fraction in the composition.

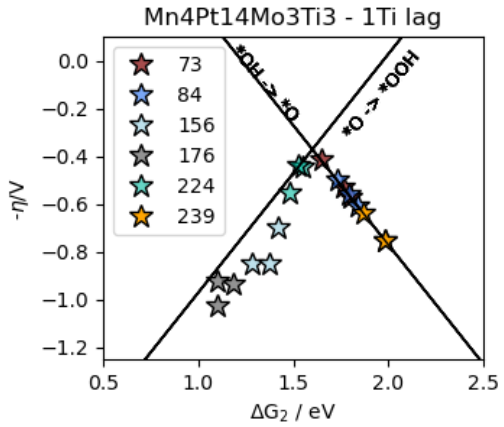

Fig. 2. Calculated activity for different Ti sites for 1 TiO2 layer on top of Mn4Pt14Ti3Mo3.

(II) Ordered mixed valence rutile oxides.

We suggest **Fe-Ta-Ti-W** combined in the following square pattern:

Ta—Ti
| |
Fe—W

With this setup both Ta^{5+} and $W^{5+,6+}$ are situated adjacent to the two low oxidation state metal ions $Ti^{3+,4+}$ and $Fe^{2+,3+}$. This allows for binary rutile structures of the types $A^{3+}B^{5+}O_4$, $A^{2+}B_2{}^{5+}O_6$, $A_2{}^{3+}B^{6+}O_6$ at the binary edges of the library (Fig. 3). Many of these binary oxides are found in the materials project database (https://next-gen.materialsproject.org/), have stabile formation energies (Energy Above Hull close to 0 eV), have small calculated bandgaps (bandgaps might be severely underestimated), have rutile structure, and have different Fermi-levels (which should allow for tunebility) (Table 1).

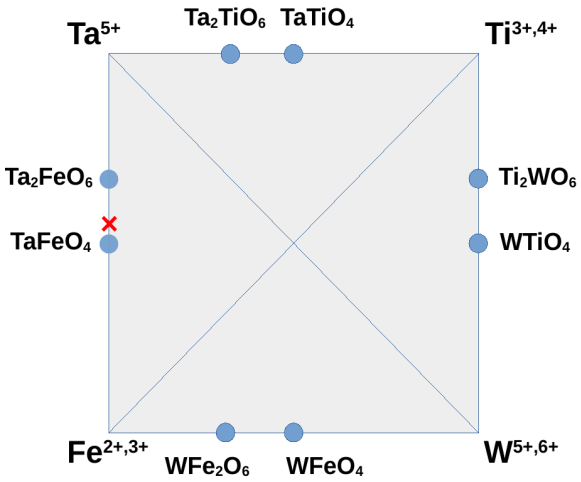

Fig. 3. Overview of possible binary rutile structures at the edges of the Fe-Ta-Ti-W. The "×" marks the TiO_2@$Ta_{1.06}Fe_{0.94}O_4$ predicted to be highly active for OER.

Table 1.

System	Energy Above Hull (eV/atom)	Band Gap (eV)	Rutile structure	Link	Fermi level, E_F - E_F^{RuO2} (eV)
Ta_2TiO_6	0.018	0	Yes	https://next-gen.materialsproject.org/materials/mp-1218045	
$TaTiO_4$	0	0	Yes	https://next-gen.materialsproject.org/materials/mp-760439	0.79
Ti_2WO_6		Not in the database			
$WTiO_4$	0.05	0	Yes	https://next-gen.materialsproject.org/materials/mp-753512	
$WFeO_4$	0	2.40	No	https://next-gen.materialsproject.org/materials/mp-19421	
WFe_2O_6	0.03	0	No	https://next-gen.materialsproject.org/materials/mp-22124	
$TaFeO_4$	0	0	Yes	https://next-gen.materialsproject.org/materials/mp-761390	-0.98
Ta_2FeO_6	0	2.06	Yes	https://next-gen.materialsproject.org/materials/mp-31755	0.30