Electronic Supplementary Material (ESI) for RSC Advances.

Oxygen reduction on nanocrystalline ruthenia - local structure effects

Supporting information

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Construction of the surface Purbaix diagrams

It is generally known that the structure of oxide based surfaces shows a pronounced potential dependence resulting from protonation/deprotonation reactions on the terminal surface oxygen atoms. The DFT analysis of the limiting barriers in oxide catalyzed processes, therefore, needs to be preceded by a determination of the most likely catalyst's surface structure. One can, therefore, follow the potential controlled evolution of the surface structures investigating the total surface energy of the possible surface structures at potential of 0 V (vs RHE) assuming that the potential dependence of the surface energy is linear and that slope of the surface energy vs. potential lines is proportional to the charge passed in the reaction describing the formation of the particular surface structure from a standard surface structure.

In the case of non-doped RuO_2 the "standard" surface represents a {110} surface featuring no oxygen atoms in *cus* positions (c) while maintaining full coverage of *bridge* (b) sites with oxygen. This surface corresponds to that shown in Figure 1S which can be also described by a notation 2c2b. This notation also reflects the size of the 2x1 surface used in the DFT calculations.

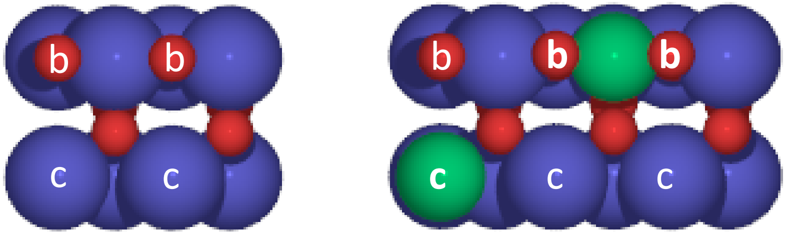

Figure 1S. Schematic representation of the {110} "standard" surface of non-doped RuO_2 (left) and Ni doped RuO_2(right). Color code: Ru-blue, O-red, Ni-green.

The considered reactions can be written as follows:

2c2b + $2H^+$ + $2e^-$ → 2c 2(b-H) (1)

2c2b + $2H_2O$ → 2(c-OH) 2(b-H) (2)

2c2b + H_2O → 2(c-OH) 2b + H^+ + $2e^-$ (3)

The binding energies as a function of the potential were were referenced to the energy of the “standard”surface, H_2 and H_2O [1]. The binding free energies calculated at potential of 0 V for reactions (1)-(3) are listed in Table 1S.

It can be easily envisaged that while the reactions (1) and (3) are of electrochemical nature and, therefore, their free enthalpy is potential dependent while in the case of reaction (2) the Gibbs free energy should be potential independent. The reactions (1)-(3) lead to surface structures denoted A-C in the Figure 9 of the main paper. The stable surface structure at any potential can be determined as the structure associated with the surface reaction yielding the highest stabilization of the system. Further DFT based investigations of the oxygen reduction were restricted to the most stable surface structure in the potential interval of electrocatalytic activity.

In the case of the doped ruthenim dioxide catalysts one needs to extend the scope of the considered surface reactions to account for the fact that the cationic position in the vicinity of *cus* and *bridge* sites may be occupied by both Ru and heteroatom, e.g. Ni. The “standard” surface for this case is shown in Fig. 1S; the corresponding notation is **c**2c**2b**b. The bold symbol denotes an oxygen position adjacent to Ni atom. Corresponding reactions are summarized in the equations (4) to (8).

c2c**2b**b + $3H^+$ + $3e^-$ → **c**2c **2(b-H)** b-H (4)

c2c**2b**b + $2H^+$ + $2e^-$ → **c**2c **2(b-H)** b (5)

c2c**2b**b + H^+ + e^- +$2H_2O$ → **c**2(c-OH) **2(b-H)** b-H (6)

c2c**2b**b +$2H_2O$ → **c**2(c-O) **2(b-H)**b + $2e^-$ + $2H^+$ (7)

c2c**2b**b +$2H_2O$ → **c**2(c-O) **(b-H)b**b + $3e^-$ + $3H^+$ (8)

The binding energies corresponding to the reactions (4)-(8) are also listed in Table 1S. All free energies are referenced to the energy of the “standard” surface, H_2 and water. The zero point energy and entropy corrections were taken from literature [2].

Table 1S Intermediate binding energies used to construct surface Pourbaix diagrams. The values were calculate at potential of 0V (vs. RHE)

RuO_2	ΔG/eV
2c2b + $2H^+$ + $2e^-$ ➔→ 2c 2(b-H)	-1.35
2c2b + $2H_2O$ → 2(c-OH) 2(b-H)	-0.08
2c2b + H_2O ➔→ 2(c-OH) 2b + H^+ + $2e^-$	1.95
Ni doped RuO_2	
c2c**2b**b + $3H^+$ + $3e^-$ ➔→ **c**2c **2(b-H)** b-H	-2.91
c2c**2b**b + $2H^+$ + $2e^-$ ➔→ **c**2c **2(b-H)** b	-2.11
c2c**2b**b + H^+ + e^- +$2H_2O$➔→ **c**2(c-OH) **2(b-H)** b-H	-1.19
c2c**2b**b +$2H_2O$➔→ **c**2(c-O) **2(b-H)**b + $2e^-$ + $2H^+$	2.05
c2c**2b**b +$2H_2O$➔→ **c**2(c-O) **(b-H)b**b + $3e^-$ + $3H^+$	3.22

References

[1] Nørskov, J.K., et al., J. Phys. Chem. B., 2004, **108**, p. 17886-17892
[2] Man, I.C., et al., ChemCatChem, 2011, **3**, p. 1159-1165