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Computational Study of the Electronic Structure of Various Cobalt (Hydroxy) Oxides in Electrolysis Reactions

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Motivation

Dr. Jon Schoer, Dr. Luke Venstrom, Dr. Robert Palumbo, and Dr. Shanin Nudehi are developing a process to use solar energy to produce H_2 gas. This process is called solar thermal decoupled electrolysis. A schematic of this process is shown in Figure 1.

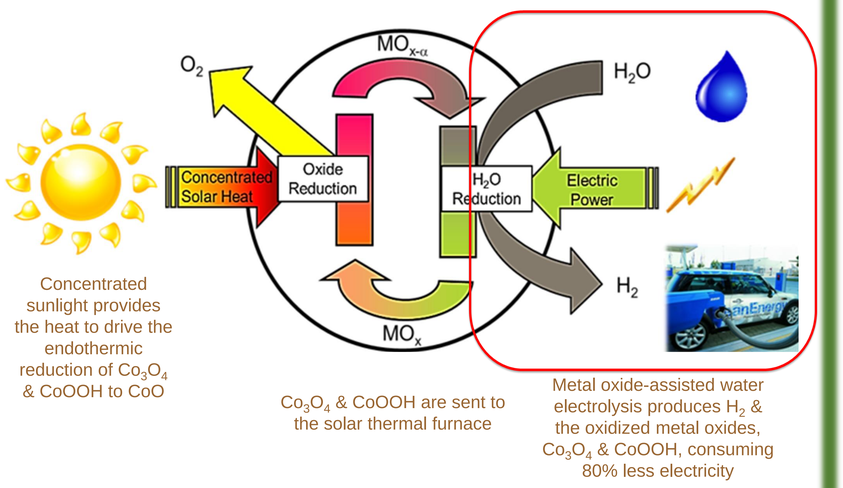


Figure 1: Complete cycle for the metal oxide-assisted, solar thermal, decoupled, electrolysis for the production of hydrogen from water.

For this process to be commercially viable, a current density of 50 mA/cm^2 must be achievable throughout the course of the electrolysis. Over summer 2018, the group working on solar thermal decoupled electrolysis was able achieve a current density of 30 mA/cm^2. Though the desired current density was not achieved, the current density was observed to grow over time. The group has shown experimental evidence to suggest that the reason that this current density is growing over time because the cobalt species being deposited on the electrode surface are acting as a new electrode surface. In attempts to validate this prediction, a computational model of this system was created.

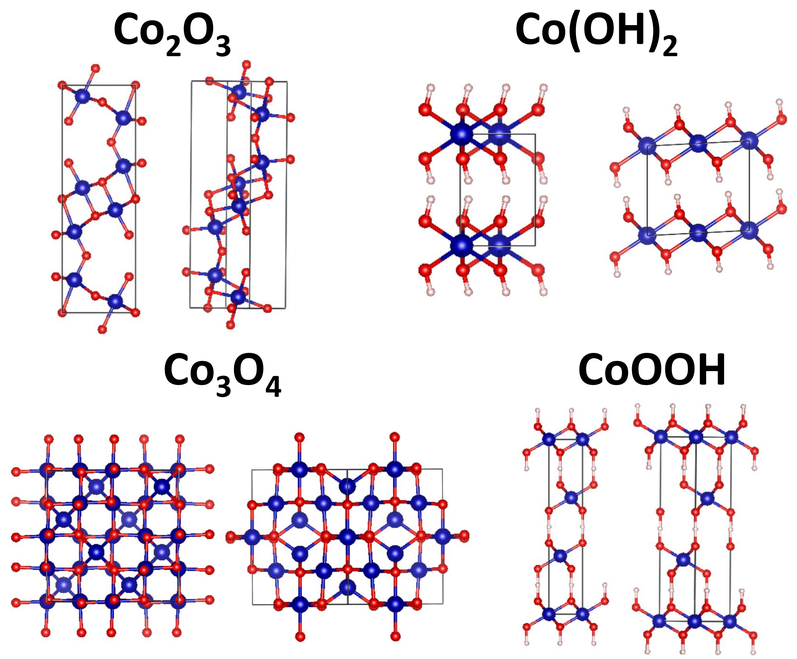
Computational Method

The structure and electronic structure of four different cobalt (hydroxy)oxide species was determined based on density functional theory (DFT)

- Vienna Ab-initio Simulation Package (VASP)
- PBE exchange–correlation functional
- van der Waals (vdW) interaction (D2 method)
- Projector augmented wave (PAW) potentials and plane waves

Optimization of Crystals

The bulk crystal structures of these cobalt (hydroxy)oxides were modeled in VASP. The optimized crystal structures are shown in Figure 2.



Figgre 2: The crystal structures of each cobalt species. The blue atoms are cobalt, the red atoms are oxygen, and the white atoms are hydrogen

Table 1: Comparison of calculated lattice parameters for each of the studied cobalt species and the values found in literature.

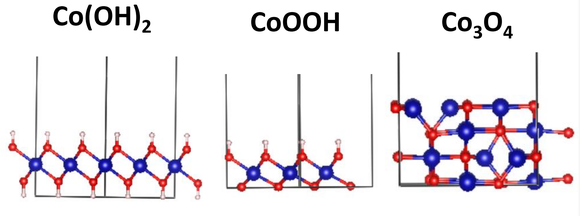
Species	Literature (Å)	This work (Å)	Percent Difference (%)
CoOOH	2.85, 2.85, 13.15	2.84, 2.46, 12.86	0.35, 13.68, 2.21
$Co(OH)_2$	5.49, 3.24, 4.81	5.31, 3.35, 4.41	3.3, 3.4, 10
Co_3O_4	8.08	7.98	1.24
Co_2O_3	3.02, 4.92, 15.22	2.79, 4.66, 14.46	7.62, 5.28, 4.99

The lattice parameters of most of the species are consistent within the limitations of the computational method.

Optimization of Monolayers

Once the crystal structures were found, the structures of each of the cobalt (hydroxy) oxides as monolayers were found.

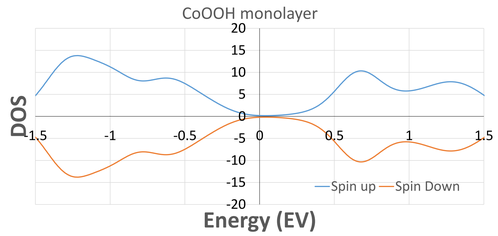
Figure 3: The structure of the monolayers of various cobalt (hydroxy)oxide species. The blue atoms are Co, the red atoms are O, and the white atoms are H.



Electronic Structures of Monolayers

Once the structure of the monolayers of cobalt (hydroxy)oxides were found, the electronic structure of each monolayer was found. The electronic structures are shown in Figures 4-6.

Figure 4: The electronic structure of CoOOH. The magnetization of this monolayer was 0 μ_B.



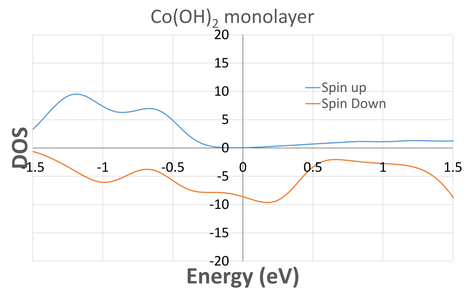
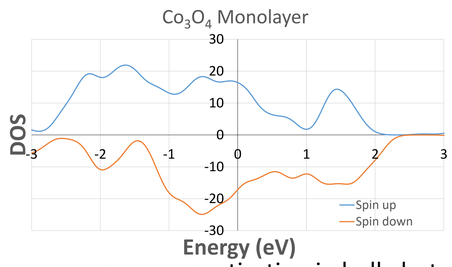


Figure 5: The electronic structure of $Co(OH)_2$. The magnetization of this monolayer was 0.74 μ_B per Co atom.

Figure 6: The electronic structure of Co_3O_4. The magnetization of this monolayer was 2.24 μ_B per Co atom.

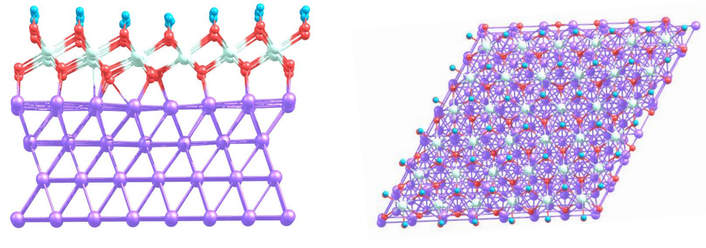


- CoOOH is a conductor and has a non-zero magnetization in bulk, but as a monolayer, CoOOH is a semiconductor with no net magnetization
- $Co(OH)_2$ is not a conductor in bulk, but as a monolayer, it is.
- Co_3O_4 is a conductor both in bulk and as a monolayer.

Monolayer of CoOOH on Ni(111)

The monolayer of CoOOH was put on a Ni(111) surface and optimized. The optimized structure of CoOOH on Ni(111) is shown in Figure 7.

Figure 7: The structure of CoOOH on a Ni(111) surface.



References

S. Grimme, "Semiempirical GGA-type density functional constructed with a long-range dispersion correction," J. Comput. Chem. **27**, 1787-1799 (2006).