Catalysis for energy storage, Final Exam

December 19, 2023
Name (First name, Last name):
Student ID number:

PCs must not be used. No material other than the exam paper is permitted.

Overall 34 points.

You can also write the answer on the back of the exam paper if you run out of space; if you choose to do so, make a clear indication in the exam paper.

You have a maximum of **105 minutes** to finish the exam.

1. Two parameters can be obtained in a Tafel equation: exchange current and Tafel slope. Exchange current is a measure of "intrinsic activity" whereas Tafel slope describes how the current varies with the application of overpotentials. A catalyst has been improved by increasing the number of its active sites. Explain how this improvement affects the exchange current and Tafel slopes. (4 points)

Increasing the number of the active site increase the exchange current, but does not change the tafel slope.

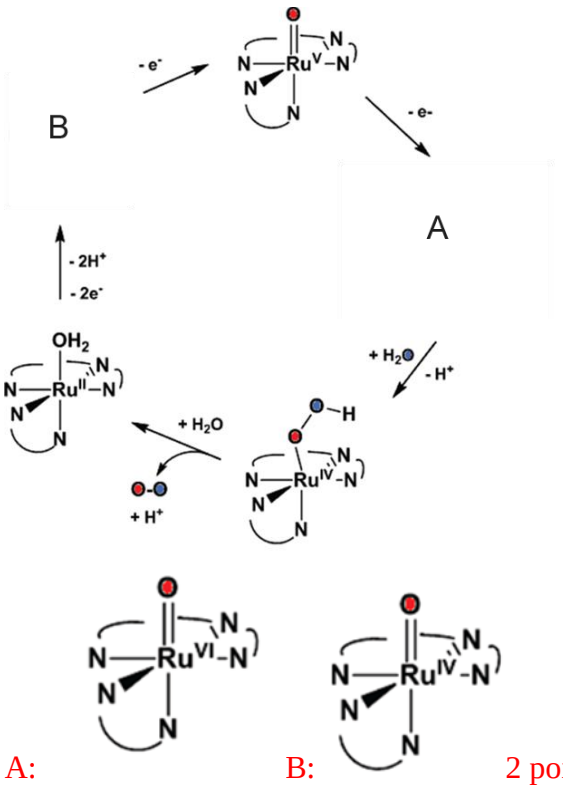
(2 points for each half part of the answer)

2. Similar to metal sulfides, metal phosphides (MP_x) have been reported as active hydrogen evolution catalysts. (a) Based on the discussion in the course about the descriptor for HER, propose a reason why metal phosphides would be a good HER catalyst. (2 points) (b) Propose two strategies to develop highly active samples of metal phosphides. (4 points)

(a) Hydrogen absorption energy is a descriptor for HER activity. Ni2P should have an appropriate hydrogen absorption energy so it can have a promising HER activity. (or something similar) (2 points)

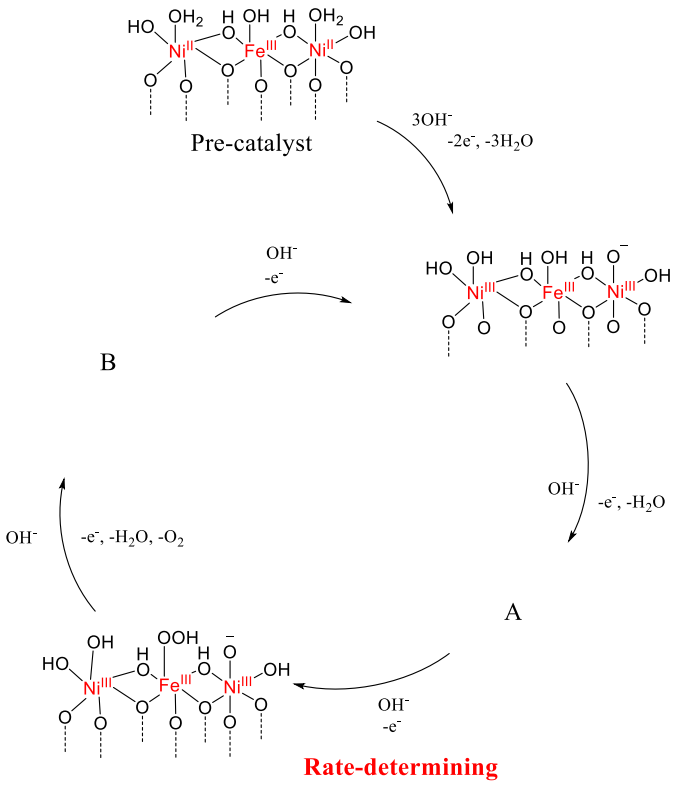
(b) Choose two of the following three:
Make high surface area nanoparticles by reducing the size
Exposing more sites
Coupling to a conductive substrate
(or increase intrinsic activity by certain methods (e.g., doping…)
2 points for each good choice. Maximum 4 points

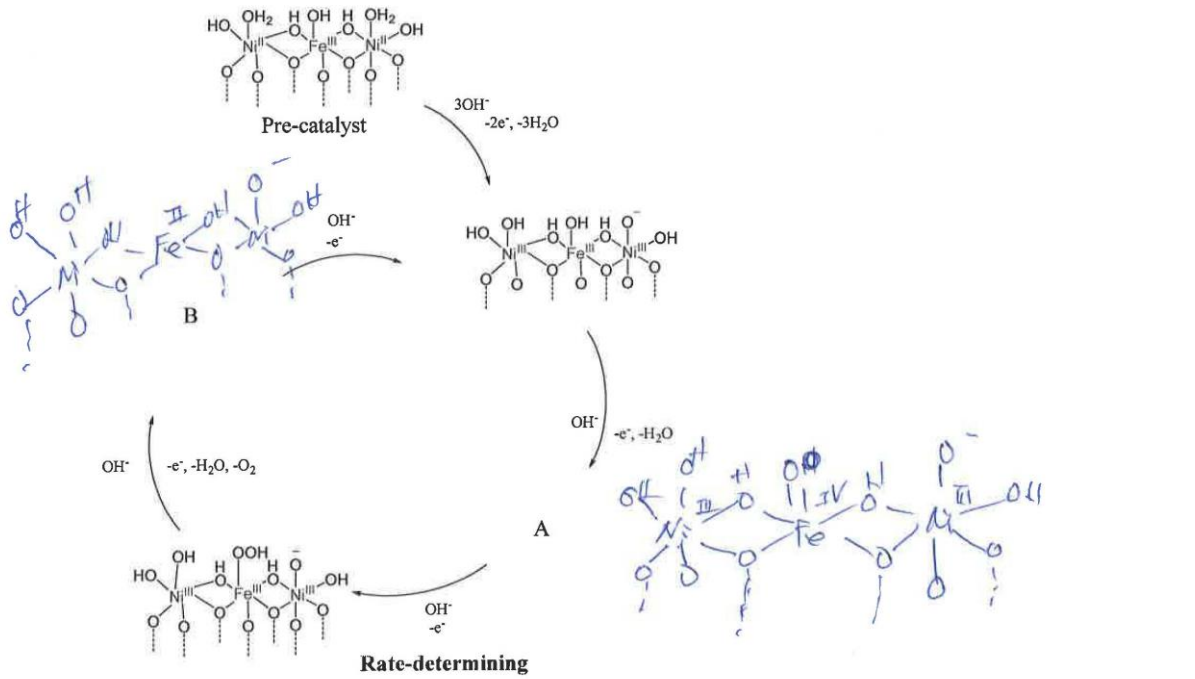
3. The following mechanism was proposed for OER catalyzed by a Ru complex. Please draw the structural formula of the missing species A and B. Please label the oxidation state of Ru. (4 points)



A: B: 2 points each; oxidation state 1 point each

4. Nickel iron oxide (NiFeOx) is a benchmark catalyst for the oxygen evolution reaction. The following mechanism is proposed for NiFeOx. Please complete the missing species (A and B) in the catalytic cycle. Label the oxidation states of Ni and Fe. (4 points)


Pre-catalyst
3OH⁻
-2e⁻, -3H2O
OH⁻
-e⁻
B
OH⁻
-e⁻, -H2O
A
OH⁻
-e⁻, -H2O, -O2
OH⁻
-e⁻
Rate-determining

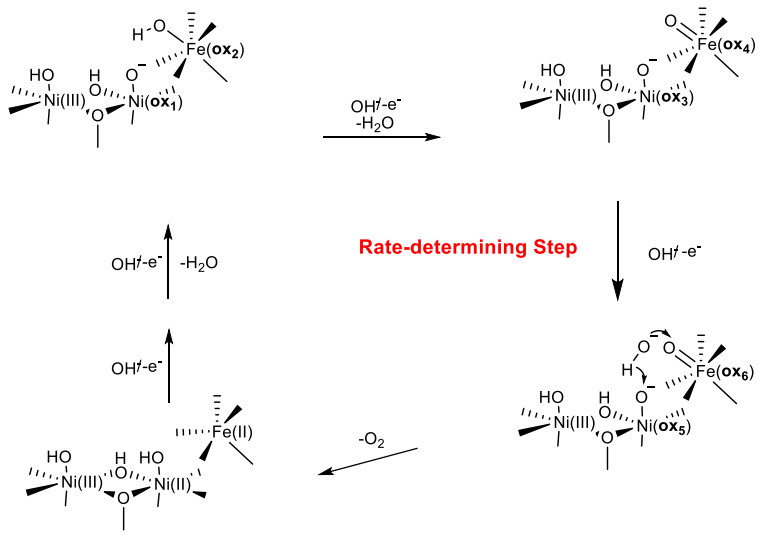


1 point each structure

1 point each oxidation state

Only if all oxidation states correct, get the point. Ni is always Ni(III)

(b) A novel catalyst, FeOOH-NiOOH, exhibits about 10-fold higher intrinsic activity than $NiFeO_x$. The following mechanism has been proposed. Please complete the missing oxidation states of Ni and Fe (ox1-ox6). (6 points)



$Ox_1 =$ III

$Ox_2 =$ III

$Ox_3 =$ II

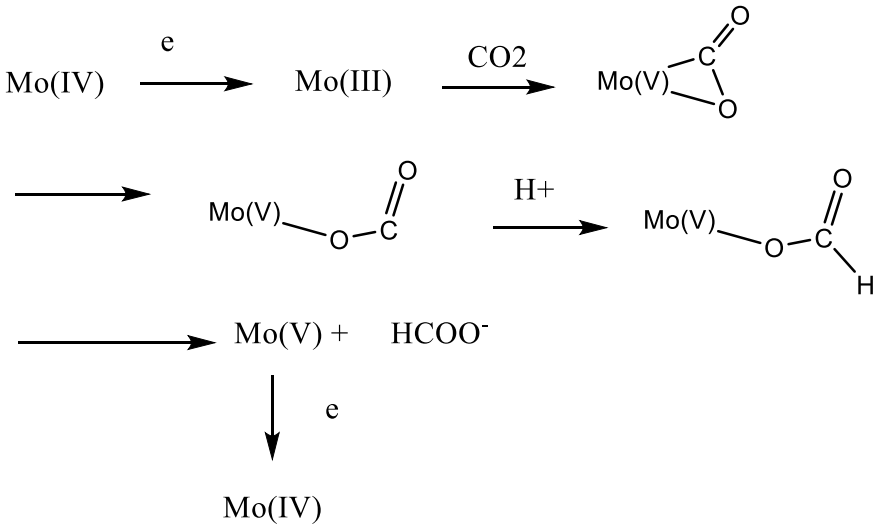
$Ox_4 =$ IV

$Ox_5 =$ III

$Ox_6 =$ ~~IV~~ V ~~IV~~ (IV would be ok considering $^{\bullet}OH$ becomes $^{\bullet}O^{-}$)

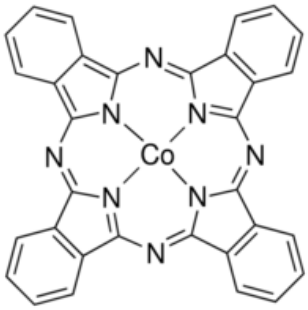
each oxidation state 0.5 points.

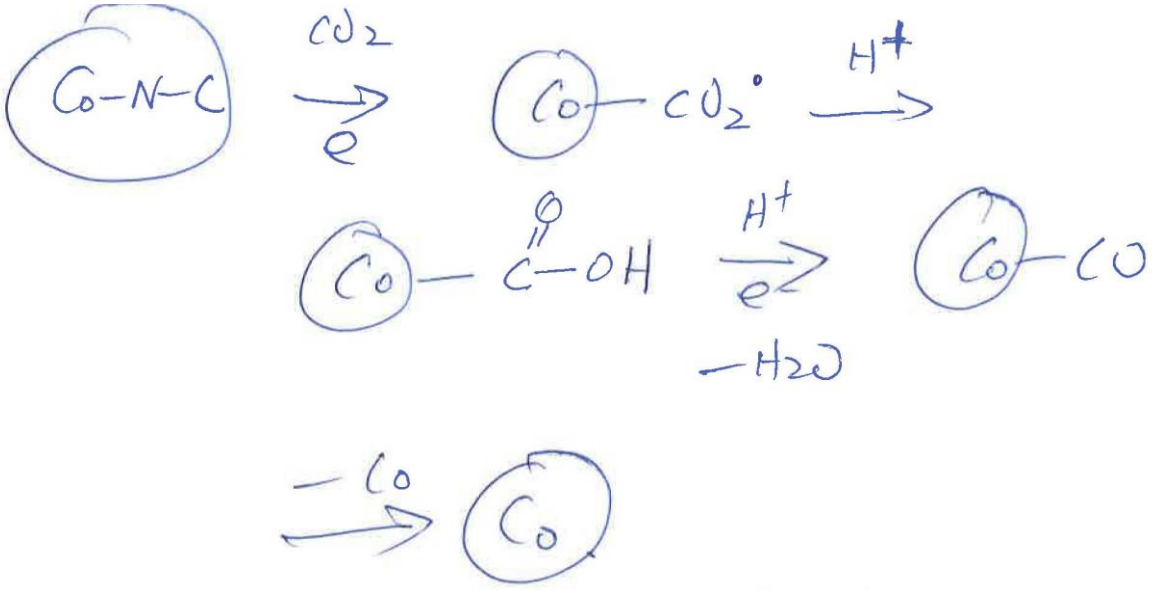
5. A molybdenum(IV) complex mimics formate dehydrogenase and can convert CO_2 and water to formate ($HCOO^-$) at pH = 7 using electrons. The lowest oxidation state of Mo in the catalytic cycle is Mo(III). Propose a self-consistent mechanism for the electrochemical reduction of CO_2 to formate by this Mo complex. The ligand of the Mo complex can be omitted. (Note: at pH = 7, formic acid exists as formate.) (6 points)



6 steps. Each step 1 point.
If the third step is not shown, and the fourth step is directly shown, it is ok.

6. Co embedded in nitrogen-doped carbon is a selective heterogeneous catalyst for the electroreduction of CO_2 to form CO. The local structure of Co is similar to Co(II) phthalocyanine (see figure below). The catalyst can be labelled as Co-N-C. It is shown that the oxidation state of Co remains as Co(II) during catalysis, and the first step is the 1-e electron reduction of CO_2 on Co without involvement of a proton. Based on this information and what you learnt from the class, propose a mechanism of CO_2 reduction to CO on Co-N-C. (4 points)





1 point for each step

Partial credits can be given if not all steps are correct.