

## **Catalysis for energy storage, Midterm Exam**

**November 6, 2024**

**Name (First name, Last name):**

**Student ID number:**

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

**Overall 30 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. (3 points)

Hydrogen storage is challenging. In addition to high pressure H<sub>2</sub> tanks, choose among the following items that can be considered as alternative H<sub>2</sub> storage methods.

- (i) Green Steel
- (ii) Green Cement
- (iii) Green Methanol
- (iv) Green ammonia
- (v) Liquid hydrogen tanks

A: (iii); (iv); (v);  
1 point each

2. (3 points) Compare the two energy storage technologies: Li ion battery and renewable fuels (including H<sub>2</sub> and other synthetic fuels). Select the technology that is stronger in each of the following three categories:

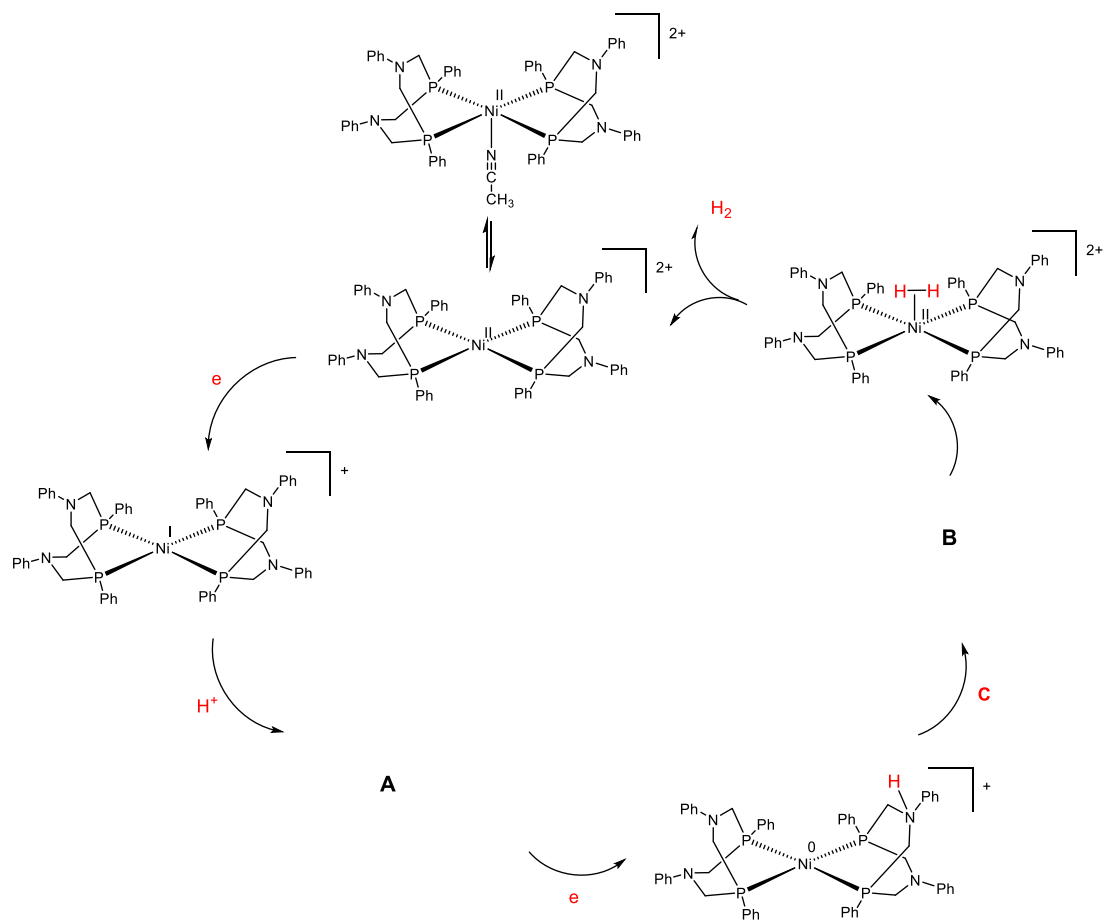
- (a) Energy density:      Li ion battery      or      Renewable fuels
- (b) Storage duration:      Li ion battery      or      Renewable fuels
- (c) Energy efficiency:      Li ion battery      or      Renewable fuels

(a): renewable fuels  
(b): renewable fuels  
(c): Li ion battery

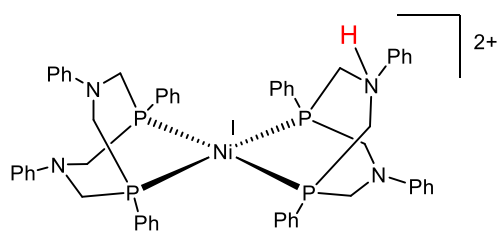
1 point each

3. (6 points) The following is a mechanism proposed for hydrogen evolution catalyzed by a Ni complex (you saw it in the class). Some part of the mechanism is incomplete.

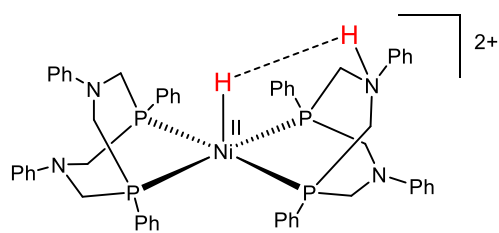
(i) Draw the structures of intermediates A and B. (ii) Label the oxidation state of the Ni in A and B. (iii) What is the reagent C? (iv) Most molecular catalysts operate at high overpotentials, but this catalyst has a high TOF at low overpotentials. Explain why this catalyst can be so efficient?



**A :**



**i) A :**



**B :**

**(OK if no**

dashed line between the two Hs)

ii) Oxidation state;  $Ni^I$  in A;  $Ni^{II}$  in B.

iii) C is  $H^+$ .

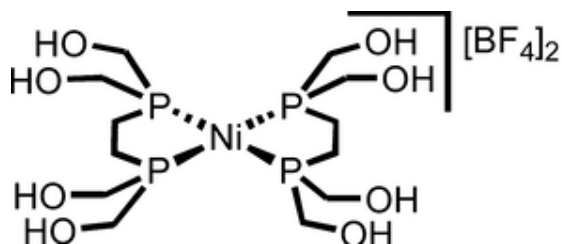
iv) Because there is a proton relay (or something along the line)

A, B, C, each 1 point.

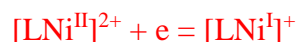
Oxidation state: 1 point each.

iv) 1 point

4. (5 points) The following complex was shown to be a molecular catalyst for hydrogen evolution in aqueous solution (pH = 1). The function of the hydroxyl groups on the ligand is to enable solubility and stability, but they are not directly involved in catalysis. It was proposed that the first step(s) of catalysis was the reduction of the Ni(II) by 2 electrons to Ni(0). Moreover, the catalysis involved only one nickel center. Based on this information, propose a reasonable mechanism for hydrogen evolution by this catalyst. Please label the oxidation state of the metal in each step. For simplicity, you can represent the starting catalyst as  $\text{NiL}(\text{BF}_4)_2$ , or  $(\text{NiL})^{2+}$ .



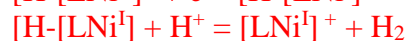
Either in equations or catalytic cycle.



2 points



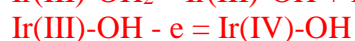
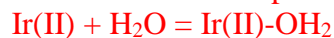
Or for the last step above:

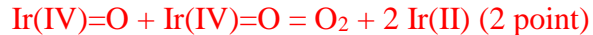


5. (6 points) An Ir(II) complex is reported as a genuine molecular catalyst for oxygen evolution at pH 0. The O-O bond forming step involves two Ir centers. The highest oxidation state of Ir in the catalytic cycle is +4. Propose a mechanism for oxygen evolution catalysed by this complex. Specify the oxidation state of Ir in each step.

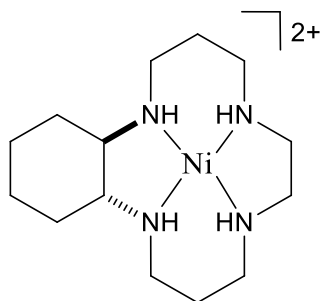
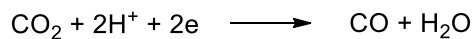
Bimetallic; each step 1 point except the last step for 2 point. Order of deprotonation is not important.

Oxidation state: 0.5 point point each.





6. (6 points) Selective electrochemical reduction of  $\text{CO}_2$  to  $\text{CO}$  in water can be achieved by the following molecular Ni complex. It is observed that the catalytic wave occurs at the  $\text{Ni(II)/Ni(I)}$  couple. Propose the catalytic cycle for the reaction. Label the oxidation state of the Ni. Propose a reason why the reaction is selective for making  $\text{CO}$ .



A :

1.  $\text{Ni(II)} + \text{e} = \text{Ni(I)}$  0.5 point
2.  $\text{Ni(I)} + \text{CO}_2 = \text{Ni(III)-CO}_2$  1 point
3.  $\text{Ni(III)-CO}_2 + \text{H}^+ = \text{Ni(III)-COOH}$  0.5 point
4.  $\text{Ni(III)-COOH} + \text{e} = \text{Ni(II)-COOH}$  0.5 point
5.  $\text{Ni(II)-COOH} + \text{H}^+ = \text{Ni(II)-CO} + \text{H}_2\text{O}$  1 point
6.  $\text{Ni(II)-CO} = \text{Ni(II)} + \text{CO}$  0.5 point

The order of proton and electron transfer (steps 3-5) can be varied.

The reason why the reaction is selective is that the H on the NH ligand can stabilize the  $\text{Ni-C(O)(O)}$  intermediate, therefore leading to selective  $\text{CO}$  formation (something along this line). 2 points