

The focus of this research is the development of organic-inorganic catalysts for electrocatalytic water oxidation reaction (OER) with their systematic structural investigation, especially their behavior in rehydration/dehydration reaction. OER is important part not just as the anodic half reaction in electrocatalytic water splitting, but also in the electrochemical reduction of CO<sub>2</sub> (CO<sub>2</sub>-RR). Both of them have significant importance in the field of energy conversion and the storage of clean energy.

As the result of my previous scholarship founded by the Hungarian American Enterprise Scholarship Found, in the first few months of my research I was continuously working on the structural characterization of copper based CO<sub>2</sub>-RR catalysts. This work led us to publish the results with success in the prestigious journal of Energy & Environmental Science (IF. 29.518) in this August. With the cooperation of my colleagues from the Lawrence Berkeley National Laboratory we developed a device that is capable to convert CO<sub>2</sub> to alcohols using sunlight with a higher efficiency than e.g. the corn itself. For the structural characterization of catalysts on both the cathodic and anodic sides we used XRD, XPS and electron microscopy techniques among others. Beside the synthesis of the Cu-Ag catalyst for the cathodic side (I fulfilled this part by the end of December of 2016) starting at January of 2017 I made the characterizations for both the anodic and cathodic part by XRD, XPS. As a result I described the surface of the CuAg nanocoral as the mixture of a cupreous oxide and carbonate phase with the presence of small amount of silver. The carbonate is represented exclusively on the surface and its presence in the bulk isn't proved by XRD. Varying the synthesis parameters such as the deposition time, beside the complexity of the structure, the Ag/Cu ratio can be also well-controlled. With the longer deposition time, metal foam like structure can be observed with a higher Ag/Cu ratio. Although the higher amount of silver is favored for the conversion of CO<sub>2</sub> to CO, therefore it has the benefit to shifting the selectivity towards to alcohols, the more complex structure can increase the effect of polarization. Overall what we developed is a solar-driven CO<sub>2</sub> reduction system which generates hydrocarbon and oxygenate products with the efficiency far higher than natural photosynthesis.

The OER has a crucial role in both CO<sub>2</sub> RR and electrocatalytic water splitting. While the acidic or alkaline pH is more favorable for the H<sub>2</sub> generation, neutral condition is necessary for the higher efficiency of CO<sub>2</sub> RR. Under acidic conditions the most active OER catalysts are the iridium and ruthenium-oxides, while in basic pH the nickel-iron layered double hydroxide (LDH) is the most effective. NiFe-LDH is a widely studied catalyst, but there are still many unanswered questions related to the reason behind its high catalytic activity. While iron has a crucial role in the elevated electrocatalytic activity in NiFe-LDH, there is no consensus over the synergetic effect between Ni(II) and Fe(III) in OER. The Fe<sub>3</sub>OH site is catalytically active in the reaction, and Fe(III) cation has a higher polarizing power than Ni(II), so the removal of charge density of oxygen increases, with the decreases of the oxygen effective charge. The rate determining step is associated to removal of proton in the layer surface, which is in correlation to the acid-base properties.

As an electrocatalyst, more attention has been focused on the Ni(II)-Fe(III) LDH that is the active species of the Fe containing Ni-based oxygen evolution catalyst (OEC) or Ni-Fe-oxyhydroxide ((Ni(Fe)OOH), which is so far the most active OER electrocatalyst under basic conditions.[7,8] The Ni(OH)<sub>2</sub>/NiOOH has a beneficial, three-dimensionally porous brucite structure that facilitates ion transport and electrical conductivity. In the brucite-like structure the Fe(III) can easily substitute for the Ni(II), forming catalytically active, structurally-stabilized Fe sites [9,10]. Previous findings have conclusively demonstrated the beneficial role of Fe in the catalytic activity of pure NiOOH [11]. Moreover, Fe(III) has been identified as the catalytically active site. One possible reason is the distorted octahedral structure, where the different Fe-O bond lengths seem to indicate that the local bond structure around the metal centers plays a crucial role in the activity.

In summary, the Ni-Fe-oxyhydroxide has high catalytic activity in OER and the Ni(II)Fe(III)-LDH phase is critical for this activity, although many questions remain about the effect of local atomic structure on catalytic activity.

In the case of OER, the surface metal cations (M) are supposed to be the active sites [12]. The reaction proceeds through a series of intermediates (e.g., M-OH, M-O, M-OOH, M-OO), all bound by a M-O bond [8]. An ideal OER catalyst should have optimal interaction with each of these oxygenated intermediate species. According to the Sabatier principle, the relationship between the M-O bond strength and the catalytic activity can be plotted on a “volcano” curve. The optimal strength of the M-O bond coincides with lower overpotential, and thus provides a fundamental material property as a descriptor for catalytic activity. By examining a series of LDHs with divalent metals other than nickel, we can explore the validity of this principle for bimetallic LDH systems. Besides Co, Fe, and Ni, Cu seems to be a potentially ideal candidate as the divalent metal. These metals have different affinities for forming metal-oxygen and metal-hydroxide bonds. The M-O and M-OH bonds with Cu(II) are stronger than those with Ni(II), while those with Co(II) and Fe(II) are weaker. Most importantly, as divalent metals, all of them can form LDH structures with Fe(III). Therefore, with the series of samples Cu(II)-Fe(III)-LDH, Ni(II)-Fe(III)-LDH, Co(II)-Fe(III)-LDH and Fe(II)-Fe(III)-LDH, where the strength of the M-O bonds are systematically altered by changing the identity of the divalent metal, we can test the validity of the M-O bond as an activity descriptor for these bimetallic systems. These results will enhance our understanding of the fundamental reasons for the high activity of the Ni(II)Fe(III)-LDH and can provide insight into underlying materials properties for design of new catalytic materials with even higher activities.

The idea behind this research was tuning the catalytic activity of LDH by varying the divalent metal beside the iron. Systematic investigation of the effect on the rehydration/dehydration mechanism and the acid-base properties can give us a better view about the correlation between structure and catalytic activity. There is another benefit varying the divalent metal in the LDH. Other metals than Ni(II) can stabilize the structure under nearly neutral conditions, therefore it is possible to widening their usability in other electrocatalytic reaction than OER. As divalent metals Cu(II), Co(II), Ni(II), Ca(II) and Mg(II) were chosen based on the different bond strengths with O and OH<sup>-</sup> and structural characteristics.

The initial plan was the synthesis of LDHs with the usual co-precipitation and the reverse micelle technique. While the preparation of catalysts via co-precipitation method was successful, there was no visible benefit of the reverse micelle method in the catalytic activity but it's rather more complicated. Synthesis of LDH is possible with hydrogen template assisted deposition (HTAD) as well. The HTAD as an electrochemical deposition method is a simple process, briefly in a two electrode electrochemical cell an electrode immersed into the solution of a metal salts. When potential is switched on the electrode the metal salt is deposited onto its surface with the accompanying of hydrogen evolution. The forming hydrogen bubbles function as a template for the metal deposition. The pore size can be tuned by the acidity of the original metal salts, while the complexity of the structure depends on the deposition time. Therefore we are working on the fine tuning of the synthesis of LDH with HTAD. We prepared the special electric cell for the synthesis and it was tested with monometallic salts and then with bimetallic salts in certain ratios. Using HTAD instead of reverse micelle technique, we can obtain a more robust catalyst with a high surface area with a much simple technique, which might have more scientific interests. As a result, we were able to obtain LDHs of NiFe and CuFe synthesize on the surface of the Carbon paper electrode (Fig. 1).

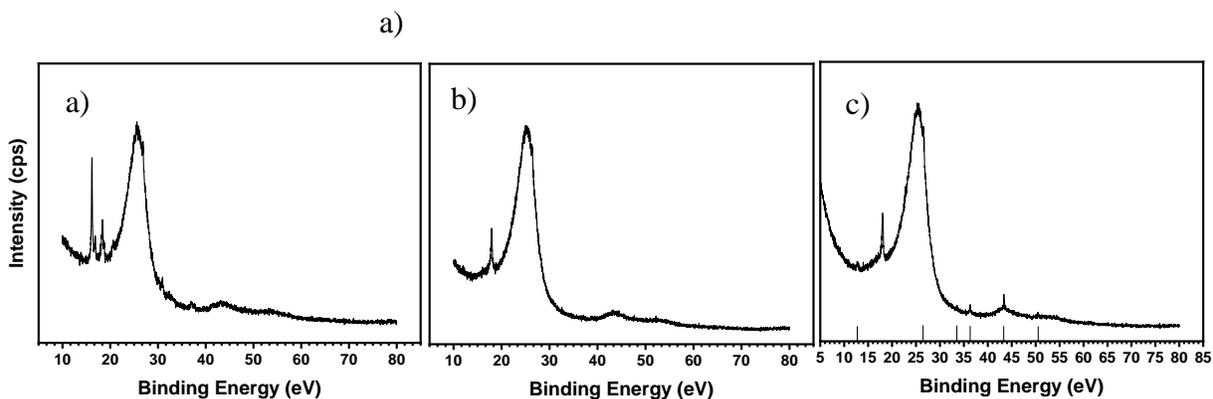


Fig. 1. XRD pattern of certain LDH synthesis with HTAD on carbon paper: a) NiOOH, b) Ni<sub>4</sub>Fe-LDH, c) Cu<sub>3</sub>Fe-LDH

LDHs for structural characterization were synthesized with co-precipitation method. The obtained electrocatalysts were investigated with XRD and in situ XPS. Temperature programmed dehydration studies showed that the removal of the interlayer water and the material stability

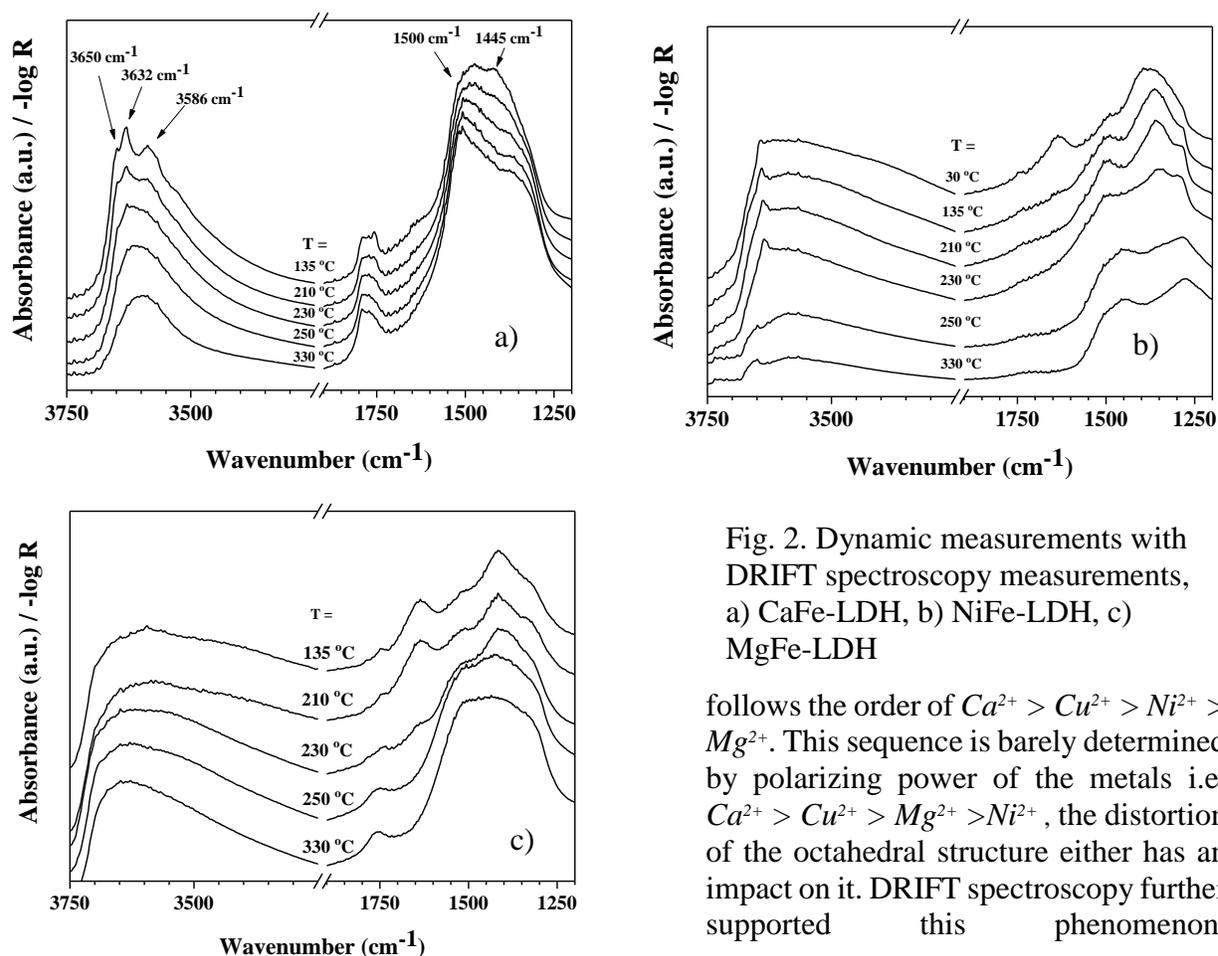


Fig. 2. Dynamic measurements with DRIFT spectroscopy measurements, a) CaFe-LDH, b) NiFe-LDH, c) MgFe-LDH

follows the order of  $Ca^{2+} > Cu^{2+} > Ni^{2+} > Mg^{2+}$ . This sequence is barely determined by polarizing power of the metals i.e.  $Ca^{2+} > Cu^{2+} > Mg^{2+} > Ni^{2+}$ , the distortion of the octahedral structure either has an impact on it. DRIFT spectroscopy further supported this phenomenon.

Furthermore the dehydration of Ni(II)Fe(III) LDH followed by DRIFT spectroscopy showed similarities with the  $\alpha$ -Ni(OH)<sub>2</sub>.

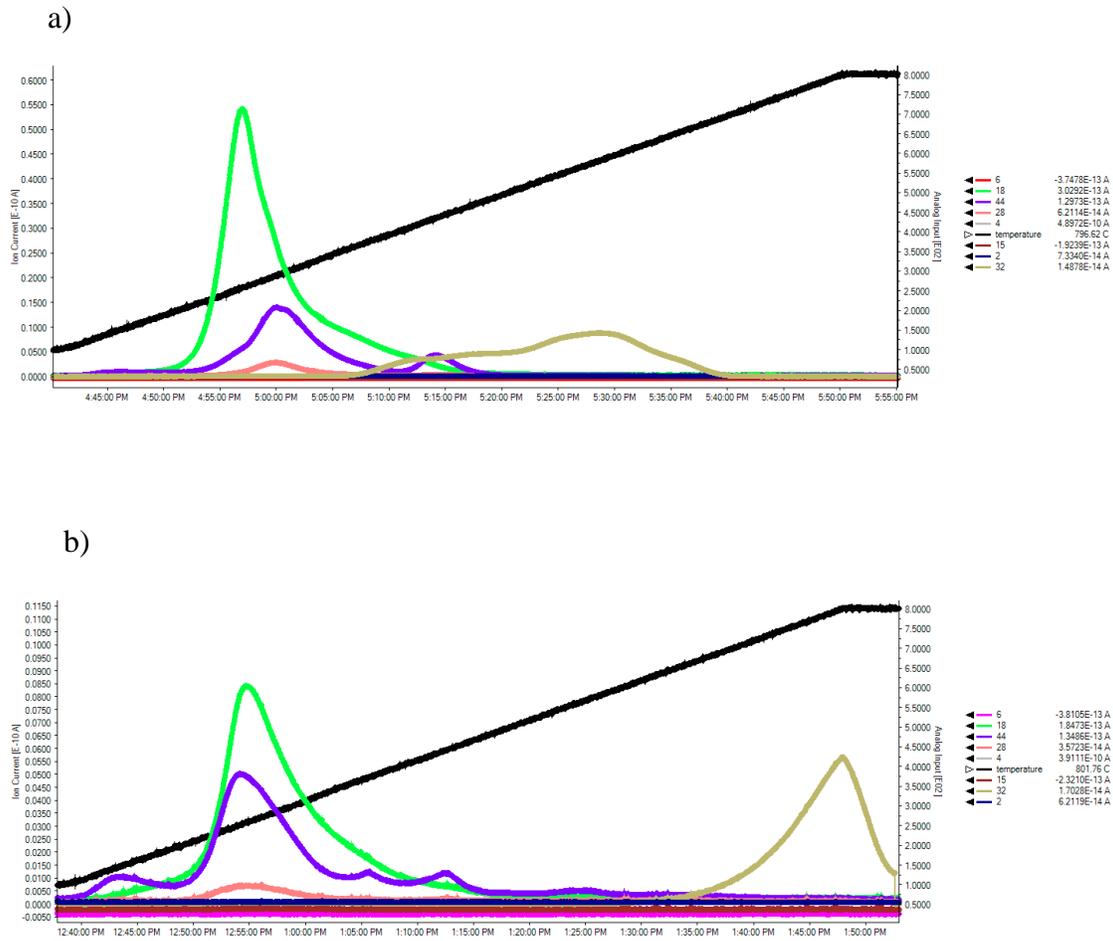
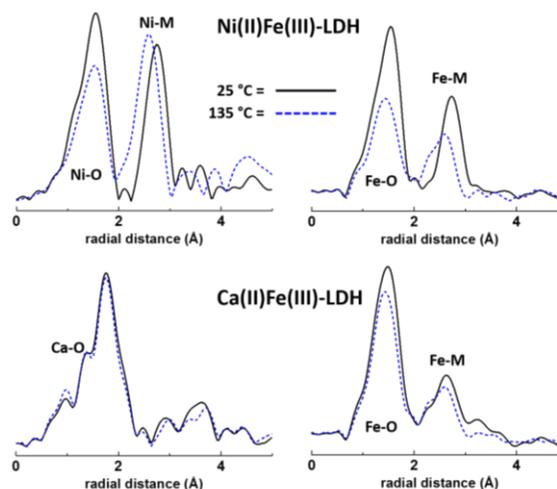


Fig. 3. Autochem measurements on a) NiFe-LDH and on b) CuFe-LDH prepared by coprecipitation. The green line corresponds to the water, the blue line to the CO<sub>2</sub>.

In the literature there is still not clear whether the nickel being crystalized in a  $\alpha$ - or  $\beta$ -Ni(OH)<sub>2</sub> phase, therefore the role of coordination of water. In the  $\alpha$ -Ni(OH)<sub>2</sub> the water molecules are weakly associated with the nickel cations and do not form hydrogen bonds with the lattice hydroxide. The rehydration of the Ni(II)Fe(III) LDH takes place due to a similar kinetics as the Ca(II)Fe(III) LDH where calcium is seven coordinated with the additional interlayer water molecule. Strengthen these observation samples were sent to the ALS in Berkeley, where AP XPS and *in situ* EXASF measurements were taken on them.

The surface composition of the catalysts and the rehydration behavior was investigated with in situ XPS, Autochem, and DRIFTS measurements. Our preliminary XAS studies at beamline 10.3.2 have already shown distinct differences in the dehydration behavior between the Ni(II)Fe(III)- and the Ca(II)Fe(III)-LDHs. In the case of Ca(II), upon removing the weakly bound structural water by heating to 135 °C, the Ca-M and Fe-M bond distances showed little change. In the Ni(II)Fe(III)-LDH, both the Ni(II)-M and the Fe(III)-M distances decreased. It is important to note that removing the weakly bounded structural water is, at least partially, a reversible process; by treating the dehydrated LDH with water vapor, the original structures may be recovered. Our preliminary results showed similarity in the rehydration kinetics of Ni(II)-Fe(III) and Ca(II)-Fe(III)-LDH, with both of these LDHs being active OER catalysts. In contrast, the rehydration behavior of Mg(II)Fe(III)-LDH was markedly different, and it was not an active OER catalyst. Thus, the ability of the LDH structure to accept water by (re)hydration may be linked to the catalytic activity.



**Figure 1** The experimental pseudo-radial distribution functions of the samples studied, Ni(II)Fe(III)-LDH and Ca(II)Fe(III)-LDH

## References

- [1] V. Balzani, A. Credi, M. Venturi, *ChemSusChem* 1 (2008) 26-58
- [2] T. J. Meyer, *Nature* 451 (2008) 778-779
- [3] D.G. Evans, R.C.T. Slade, *Struct. Bond.* 119 (2006) 1.
- [4] A. Vaccari, *Catal. Today* 41 (1998) 53.
- [5] R. Allmann, *Acta Cryst. B* 24 (1968) 972.
- [6] M. Gong, Y. G. Li, H. L. Wang, Y. Y. Liang, J. Z. Wu, J. G. Zhou, J. Wang, T. Reiger, F. Wei, H. J. Dai, *J. Am. Chem. Soc.* 135 (2013) 8452-8455
- [7] I. C. Man, H. Y. Su, F. Calle-Vallejo, H. Hansen, J. I. Martinez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Norskov, J. Rossmeisl, *ChemCatChem* 3 (2011) 1159-1165
- [8] M. E. G. Lyons, M. P. Brandon, *Int. J. Electrochem. Sci* 3 (2008) 1386
- [9] L. Trotochaud, J.K. Ranney, K.N. Williams, S.W. Boettcher, *J. Am. Chem. Soc.* 134 (2012) 17253–17261.
- [10] Trotochaud, S. L. Young, J.K. Ranney, S.W. Boettcher, *J. Am. Chem. Soc.* 136 (2014) 6744
- [11] S. Klaus, Y. Cai, M. W. Louie, L. Trotochaud, Alexis T. Bell, *J. Phys Chem C* 119 (2015) 18303-18316
- [12] Rossmeisl, J.; Qu, Z.-W.; Zhu, H.; Kroes, G.-J.; Nørskov, J. K. *J. Electroanal. Chem.* 607 (2007) 83–89