Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: **Electrodeposition of Fe(Co, Ni)-based Compounds on Porous Materials in Ionic Solutions (or Deep-eutectic Solvents) and their Electrocatalytic Properties**

Keywords: electrodeposition, ionic liquid, deep-eutectic solvent, metal co-deposition,

Joint supervision: yes (Vincent VIVIER) /~~no~~

Joint PhD (cotutelle): ~~yes (name/surname)~~ /no

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Doctoral school (N°+name): ED ED 388 Chimie Physique et Chimie Analytique de Paris-Centre

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Subject description (2 pages max):

1) Study context

Hydrogen is attracting stronger interest as clean energy vector with high energy density and low emissions[1]. The water splitting is considered to be one of the most promising solutions for the preparation of CO_2-free hydrogen. In addition, hydrogen produced by the electrolysis of water is of high purity, involving safe and simple process[2]. The electrode material is the key to the electrolysis of water. The performance of the electrode determines the cell voltage and energy consumption[3]. Pt group metals show strong catalytic performance for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), but their high costs limit their used. Therefore, the preparation of highly efficient non-noble metal catalysts for HER and OER (reactions below) is currently a hot research topic.

(HER) $2H^+ + 2e^- \rightarrow H_2$ (OER) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

In the recent years, alloying has been shown to be an important method to improve catalyst activity of the electrode. Alloys with transition metal and the heterostructures of its compounds such as Ni-, Fe-, Co-based intermetallics have been widely studied as effective bifunctional electrocatalysts. A tunable approach for surface modification consists in the use of electrodeposition for the preparation of alloys on the surface of the electrode. Interestingly, some of these alloys such as Ni-Fe-P, Ni-Mo-Fe, Ni-Fe-S, etc., exhibit excellent electrocatalysis performances[4,5]. For instance, Ni-Fe-P alloy requires a low voltage of 1.62 V to achieve 10 mA cm^{-2}, which is comparable to the commercial Pt/C//Ir/C couple (1.65 V). These good performances were ascribed to the synergistic effect of the transition metal elements and intermetallics, such as metal selenides, oxides, chalcogenides, borides, and phosphides. For the electrocatalyst prepared by electrodeposition, it is worth studying the influence of the relative amount of the elements, but also the influence of the nature of the solvent.

Recently, ionic liquids (ILs) have been studied in many chemical areas due to their interesting physicochemical properties. For instance, when compared with traditional electrodeposition in aqueous solution, the effect of water can be avoided so that the co-product can be better controlled. As highly efficient media, ILs have also been used for the electrodeposition of metal particles[6], such as Au, Cu, Fe and Ni which were prepared as electrocatalyst on the surface of an inert matrix[7]. Some alloys can also be deposited, such as Co-Al[8], Ni-Al[9], which show potential for electrocatalysis applications. Moreover, a series of transition metal selenides, metal oxides, chalcogenides, borides, and phosphides[10] can be used as symmetrical bifunctional catalysts for the water splitting. Thus, it has been shown that cobalt oxide films prepared by electrodeposition in ethylammonium nitrate, a protic IL, exhibit a considerable catalytic activity towards the electrocatalytic water oxidation reaction[11]. Some other compounds such as FeOOH, NiOOH[12], Fe_2O_3, have also been proved to be good electrocatalysts[13]. Therefore, a way forward is to combine alloys and intermetallics with porous materials by the preparation of well-designed NPs electrodeposited from IL solutions, thus expending the specific surface area, to improve the efficiency of the water splitting.

2) Details of the proposal

The main objective of this project is to provide a new and inexpensive way for the preparation of bifunctional catalysts on porous materials for the water splitting. For that, efficient metal-based catalysts based will be electrodeposited on porous materials in ionic liquids or deep-eutectic solvent for water electrolysis. In order to achieve this objective, we will choose suitable ionic liquid and compare different parameters for the electrodeposition. The physicochemical characterizations of ionic media and the electrochemical behaviour of various metal elements will be considered. Different combinations of solvent and electrodeposition parameters will bring different effects. The effect of the additional elements, the morphologies of the products controlled by the electrodeposition and the size of the grains can be the important points for the water electrolysis.

This exploration will be divided in several parts:

1. Selection and syntheses of ILs and its characterizations. Protic ionic liquids (PILs) seem to be good candidate for the electrodeposition of metal and metal oxide[11]. They exhibit better results

towards electrodeposition than aprotic ionic liquids. Two families of PILs (alkylammonium, pyrrolidinium) with different anions will be studied. Their selection will depend on the Fe, Zn, Mg, Al, Ni, Co salts dissolution.

2. The influence of different factors on the electrodeposition of Fe (Ni, Co)-based alloys and compounds on the surface of porous materials (such as aluminium foam, nickel foam, copper foam and other porous alloys), the co-deposition of light metal elements (such as Zn, Mg, Al) will also be considered;

3. The impact of different product morphologies growing through electrodeposition on the electrolysis of water;

4. The impact of different sizes of the grains/agglomerates after heat treatment on the electrolysis of water.

3) References

1. J. Yan, Z. Yao, M. Jaroniec and Z. Q. Shi, *Chemical Society Reviews*, 2015, **44**, 2060-2086.
2. X. Zou and Y. Zhang, *Chemical Society Reviews*, 2015, **44**, 5148-5180.
3. E. A. Hernández-Pagán, N. M. Vargas-Barbosa, T. Wang, Y. Zhao, E. S. Smotkin and T. E. Mallouk, *Energy & Environmental Science*, 2012, **5**, 7582-7589.
4. J. Lian, Y. Wu, H. Zhang, S. Gu, Z. Zeng and X. Ye, *International Journal of Hydrogen Energy*, 2018, **43**, 12929-12938.
5. I. Arulraj, *Bulletin of Electrochemistry*, 1999, **15**, 519-523.
6. F. Endres, M. Bukowski, R. Hempelmann and H. Natter, *Angewandte Chemie International Edition*, 2003, **42**, 3428-3430.
7. M. Asnavandi and C. Zhao, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 85-89.
8. R. T. Carlin, P. C. Trulove and C. Hugh, *Journal of The Electrochemical Society*, 1996, **143**, 2747-2758.
9. T. Moffat, *Journal of the Electrochemical Society*, 1994, **141**, 3059.
10. J. M. V. Nsanzimana, L. Gong, R. Dangol, V. Reddu, V. Jose, B. Y. Xia, Q. Yan, J. M. Lee and X. Wang, *Advanced Energy Materials*, 2019, 1901503.
11. B. H. Suryanto, X. Lu, H. M. Chan and C. Zhao, *Rsc Advances*, 2013, **3**, 20936-20942.
12. D. Friebel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng and R. Alonso-Mori, *Journal of the American Chemical Society*, 2015, **137**, 1305-1313.
13. L. Pan, J. Tang and F. Wang, *Open Chemistry*, 2013, **11**, 763-773.

4°) Profile of the Applicant (skills/diploma…)

The PhD candidate should hold a Master degree in Physical Chemistry or Electrochemistry. A high level in English or French is mandatory.

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