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CO2 reduction on post-transition metals and their alloys: an industrial approach

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Summary and future perspectives

Summary

In recent decades an increasing attention has been focused on the potentially devastating effects of climate change. Currently, it is hoped that by reducing the emissions of CO₂ to zero within 2050, it will be possible to limit the increase in average global temperatures to 1.5 °C, thereby curbing the worst possible consequences. The technological and systemic changes to be implemented to achieve this objective will have to be drastic. Among these, the transition to renewable energies, electrification of industry, use of bio-based feedstocks and the capture, storage and utilization of CO₂ are expected to play a prominent role. At present, every year, about 200 million tonnes of CO₂ are utilized by industry and about 42 billion tonnes are released by human activities in the atmosphere. It is clear that no single solution will be able of solving the problem by itself. With this in mind, and the perspective of renewable energy becoming more affordable, it makes sense to widen the portfolio of CO₂ utilization technologies with the development of industrial electrochemical CO₂ conversion.

In this thesis, with this perspective of aiming for an industrial application of CO₂ electroreduction and taking into account the principles of green chemistry whenever possible, we look at the synthesis, characterization and performance towards CO₂ electroreduction of mono and bi-metallic particles based on p-block metals. The decision to revolve around p-block metals stems from their high selectivity towards formate, a product that, on top of having already a significant market, could be used as an energy carrier and as a building block for sustainable polymers. Converting CO₂ to formate also has a high atom efficiency and can achieve high productivity with relatively low currents due to the small amount of electrons exchanged.

In chapter 2, we give an overview of some physical and chemical characteristic of post-transition metals and how these influence their application in the field of catalysis, electrocatalysis and material synthesis. We show that post-transition metals can be used in several applications of both thermal and electro-catalysis as promising

materials, able to catalyze reactions of economical as well as environmental relevance, both alone and in combination with zeolites and transition metals. On top of this, we introduce the formation of Zintl phases between post-transition elements and alkali and alkali-earth metals and describe the potential of these compounds for material synthesis.

In chapter 3, we show that it is possible to generate metallic powders based on Sn and Pb starting from a metallic plate or wire by cathodic polarization in an appropriate electrolyte. We also demonstrate that it is possible to produce a catalyst based on an alloy of Sn and Pb retaining the composition of the parent wire. This cathodic disintegration process goes through the pulverization of the cathode and is extremely quick and clean, giving stable suspensions just by carefully choosing the nature and concentration of the electrolyte. This avoids the use of organic solvents, additives, stabilizers and reducing agents. The materials obtained are tested in a Gas Diffusion Electrode flow cell and show high selectivity towards the reduction of CO₂ to formate. In chapter 4, delving into the possible causes behind the cathodic disintegration of Sn and Pb, we propose that the process is mediated by the electrochemical formation and quick decomposition of Zintl phases. The electrochemical synthesis of Sn and Pb based Zintl phases in organic solvents is a known process and can yield compounds that remain stable for some time. Despite this, Zintl phases tend to be extremely unstable when exposed to oxygen and moisture, oxidizing to the metallic state. In the case of cathodic disintegration in water, the Zintl phases would be short-lived and quickly decomposed, leading to the observed disintegration of the electrodes. In this chapter we also show the fascinating restructuring of Pb electrodes and speculate that they could be deriving from the oxidative polymerization of Zintl cluster anion starting monomers, a known process already used in material synthesis.

In chapter 5 and 6 we describe the behavior of Pd-In nanoparticles in the range of about 3.5-4 nm for the electrochemical reduction of CO₂. On In the reduction to formate proceeds through a high overpotential pathway involving a CO₂⁻ radical anion, possibly partially stabilized by

surface metastable oxides and hydroxides. On Pd, instead, the reduction to formate happens at almost no overpotential and is thought to be mediated by the insertion of CO₂ in the Pd-H bond of electrochemically generated hydrides. At higher potentials, Pd is more selective to CO and its surface is generally heavily poisoned by it. It is known that Pd and In can form several different phases according to the ratio of the two elements, ranging from solid solutions to intermetallic compounds. In particular, in chapter 5 we focus on the behavior of In-rich particles for the reduction of CO₂ to formate. We show that the interaction of In and Pd is detrimental to the selectivity towards formate of these catalysts. When mixed together, In seems to weaken the interaction of CO₂ with the surface, preventing CO poisoning and electro-hydrogenation altogether. This causes the Pd sites in Pd-In catalysts to evolve hydrogen freely even in CO₂ saturated environments, making all the current go through this reaction and impeding the high overpotential electron transfer on In from happening. Instead, in chapter 6, we show the behavior of Pd-rich nanoparticles for the electrochemical reduction of CO₂ to CO. Through experiments and DFT simulations, we show that the interaction of In and Pd in Pd-In bimetallic catalysts can change dramatically the selectivity of the electroreduction of CO₂ depending on the catalytic phase. We range from formate on In, to HER on Pd-In intermetallics and finally to CO evolution on Pd and Pd-In solid solutions.

Finally, in chapter 7, we present a physico-chemical characterization of Avantium's In-Bi catalyst for the reduction of CO₂ to formate. We show that these In-Bi catalysts are slightly more selective than In-only catalysts and markedly more selective than Bi-only catalysts prepared with the same method. We propose that this effect may be due to the fact that Bi, in a process similar to galvanic corrosion, increases the fraction of In in its oxidized state, a process that induces the segregation of this metal to the surface of the particles. The particles with a surface enriched in indium oxides can be more selective since this phase has been shown to be the most active for CO₂ reduction to formate. In addition to this, we optimize a catalyst layer investigating several parameters to achieve very high selectivity to formate at high

current density and investigate the performance degradation of our electrodes over the course of several days.

Future perspectives

In the future, several problems will have to be addressed in order to make the electrochemical reduction of CO₂ industrially appealing. The most pressing problem at present is the electrolyzer lifetime. This needs to be extended in the range of thousands of hours, which can be achieved by working on critical points like catalyst layer engineering and membrane optimization. On top of this, capital expenditures need to be addressed. Using inexpensive materials and cheap synthesis methods for the catalyst as well as trying to innovate the fabrication of ion exchange membranes in order to decrease their cost might have a positive influence on the large-scale adoption of CO₂ electroreduction technologies. Moreover, mass production of electrolyzers once the process is established, will abate costs. Talking about operational costs, instead, the main working point will be the cell voltage. This, at present, can be minimized mostly through cell design, choice of electrolytes and possibly by selecting an anodic reaction alternative to oxygen evolution. Despite the fact that the thermodynamic potential for the CO₂ reduction is similar to that of water reduction, the only materials able to retain selectivity at high current density have typically very large overpotentials for the reaction, up to 1V. Finding alternative materials able to carry out the reduction selectively, for an extended time and with lower overpotential will contribute to the adoption of this process industrially, hopefully helping in the creation of a large scale, clean CO₂ utilization platform.

