Superparamagnetism Assisted ORR on core-shell Octahedral catalysts for Fuel cells

Abstract

One of the bottlenecks towards the successful implementation of proton exchange membrane fuel cells (PEMFCs) is the high overpotential of the electrocatalytic oxygen reduction, which currently relies on a high non-sustainable loading of precious group metals.

This proposal aims at the exploration of superparamagnetism assisted electrocatalysis for the oxygen reduction on magnetic core platinum shell. These core-shell present several advantages, among them the low amount of platinum, the very mass activity measured for the Pt skin and the ability to expose the most active crystallographic planes (111 facets in octahedral nanoparticles). The magnetic properties of the core (a Ni, Co or Fe Pt alloy) has not harvested so far. Our assumption is that the magnetically induced local heating can overcome the current limitations of ORR electrocatalysts by fostering the reaction kinetics.

We shall start the project by the exploration of octahedral PtNi nanocrystals electrocatalytic activity. As previously reported, this type of electrocatalyst displays the highest intrinsic activity, even without an alternative magnetic field. We have found a synthetic pathway towards Pt {111} surfaces on a superparamagnetic Ni core (as well as Fe or Co), i.e., octahedral Ni-rich core-Pt rich shell. The catalysts already display state-of-the-art activity for acidic ORR reactions.

1. Scientific impact

The achievement of superparamagnetism induced electrocatalysis has the potential to lead to a breakthrough in the field of electrochemistry in general[1] and fuel cells in particular. The discoveries in earth abundant electrocatalysis have been remarkable during the last decade, and the progress is in overpotential reduction now measured in millivolts. The concept proposed here is expected to yield hundreds of millivolts of improvement of the overpotential. The progress in the synthesis of core-shell systems on a magnetic core could also benefit to the field of catalysis.

The technological and societal aspects of this research are multiple; the energy efficiency of power sources will benefit from the proposed fundamental research. The demonstration of low precious metals ORR electrocatalysts will be relevant to the current generation of PEMFCs, while the progress on ORR electrocatalysts will be beneficial for the next generation of non-precious catalysts.

2. Working Hypothesis

The superparamagnetism induced electrocatalysis requires the synthesis of magnetic nanoparticles with a magnetic core and a catalytic surface. The huge potential of this process in terms of energy efficiency is counter-balanced by the need for highly specific catalysts specially designed to combine high magnetic heating efficiency and good catalytic activity. Although a few phases could display both properties, we believe a more general approach would be to direct the synthesis of core-shell systems where the core and shell can be chosen almost independently to provide an optimized magnetic and catalytic behavior for each phase. The synthesis of core-shell systems has been well developed during the last decade in the literature and in our laboratory.

3. Experimental Design and Methods

a) Synthetic routes of superparamagnetic electrocatalysts

Synthesis of Ni, Co core Pt shell nano-octahedra for ORR electrocatalysis
State-of-the-art: Although nickel does not have a high magnetic, catalytic efficiency, Pt {111} skin on Ni displays the highest ORR activity known today.

The use of colloidal routes has proved to be very efficient in order to synthesize metallic NPs with a clean metallic surface.[2,3],[4] Preferential ligands adsorption can direct the nanocrystal growth with a specific shape and crystallographic planes forming the facets, like {111} in the case of Ni.[5]
Galvanic replacement reaction (GRR) can generate core-shell bimetallic nanoparticles.[6],[7] GRR can convert monometallic nanostructures into complex multimetallic structures, using one or several steps to yield multimetallic colloids.[8] Our group has recently observed the tip-enhanced growth of noble metal on Ni faceted nanocrystals.[9]
On the other hand, the one-pot reaction can also yield core-shell nanoparticles, in the case of thermodynamically-induced phase segregation or with the kinetically driven formation of core-shell systems. This approach has been successfully applied to the formation of Ni core Pt shell nano-octahedra (see preliminary results below).

4. Preliminary Results

Solvothermal synthesis of Pt-Ni nanoparticles yields 5.1 +/- 0.5 nm truncated octahedral PtNi nanoparticles. The synthesis has been modified from the literature[10–12] and our previous publication[13] by adjusting the reaction kinetics and promoting the segregation of Ni at the center of the nanocrystal. The nanocrystals have a core-shell structure as evidenced by high-angle annular dark field imaging and energy dispersive X-ray spectroscopy (EDX) mapping and line scan. The magnetic properties reflect mainly the presence of a superparamagnetic core with a spontaneous magnetization corresponding to Ni metal while the Pt shell shows a very high activity compared to Pt dispersed on carbon.

Conclusion

This scientific project aims at the exploration of superparamagnetism assisted electrocatalysis. For this purpose, this proposal innovates with original core-shell systems with a high magnetic moment in the core and high electrocatalytic activity of the shell. The concept proposed there expected to yield a significant decrease of the overpotential. The extent to which the catalytic activity can be enhanced by the induction effect, and the local temperature increase on the catalyst surface caused by said effect, will be investigated by the proposed research; as well as how the selectivity changes due to amplification effect.

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