

Modified Substrates for Oxygen Reduction Reaction

C. Zafferoni^{a,†}, M. Innocenti^{a,b,*}, G. Giambastiani^b, G. Tuci^b, L. Becucci^a, F. Capolupo^a and M.L. Foresti^a

^aDepartment of Chemistry, University of Florence via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy.

^bInstitute of Chemistry of OrganoMetallic compounds ICCOM-CNR via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy.

Nowadays, electrochemistry extends to the domain of material science because of the development of electrochemical methods for the electrodeposition of materials controlled down to atomic level. Electrocatalysis is largely employed for the coating of surfaces with metals able to exert catalytic effects in specific processes. The occurrence of synergistic effects between different metal layers are expected to play a role in important electrochemical reactions like the Oxygen Reduction Reaction (ORR). ORR is regarded as one of the most important electrocatalytic reaction operating in energy conversion devices (fuel cells) as well as in important industrial processes. In spite of the many attempts made in the last decade to create Pt-free catalysts for low temperature air cathodes, Pt remains the metal of choice at least for fuel cells operating in acid environments. In alkaline fuel cells where the flexibility concerning the cathode catalyst is much larger, Pt-free catalysts based on Ni, Ag, Co can be used. Even if these metals should not be considered non-precious metals, electrodeposition represents a good method for controlling and limiting the amount of deposited metals through either the use of the Faraday's law or the use of self-limiting phenomena such as those involved in underpotential deposition (UPD) [1]. On this ground, a good compromise between metal cost and catalyst performance is represented by the use of small quantities of catalysts and the development of new methods able to modify the structure of the deposited metals increasing the number of active sites. Some of us have recently proposed a method for the modification of noble metal surfaces, denoted as ElectroChemical Milling and Faceting (ECMF). This approach has shown how the catalytic properties of Pt-nanoparticles could be enhanced by one order of magnitude for the ethanol electrooxidation after milling and faceting actions [2]. Following a similar approach we have studied the catalytic properties of small ($3\text{-}17\ \mu\text{g cm}^{-2}$) quantities of silver microparticles electrodeposited on glassy carbon electrodes before and after an electrochemical oxidative/reductive protocol in alkaline media. Such an approach which involves the formation and subsequent reduction of the silver oxide, has resulted in more effective catalysts for the ORR. The modification of the surface active sites, their morphological properties (surface roughness) and their catalytic performance in ORR will be properly discussed.

[1] D.M. Kolb; in *Advances in Electrochemistry and Electrochemical Engineering*, Gerischer, H.; Tobias, H.; Eds.; vol 11, John Wiley, New York, (1978) 125.

[2] Y. X Chen., A. Lavacchi, S. P. Chen, F. Di Benedetto, M. Bevilacqua, C. Bianchini, P. Fornasiero, M. Innocenti, M. Marcello, W. Oberhauser, S. G. Sun, F. Vizza, *Angew. Chem., Int. Ed.*, 51 (2012) 8500-8504.

* The Electrochemical Society Active Member

† claudio.zafferoni@unifi.it