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Preparation of powder catalyst inks in hydroalcoholic solutions using an ultrasonic bath (SONICA 3200 EP) for coating glassy carbon rotating disk electrodes for electrochemical measurements

The goodness of electrochemical measurement on heterogeneous catalysts, in powder form, cannot ignore the preparation of a homogeneous and reproducible layer on an electrode. The electrochemistry laboratory of Chemical Sciences of the University of Padua performs measurements on several types of catalysts, i.e., carbons, Pt/C, or MoS_2, and needs a way of producing homogeneous, controllable, and reproducible dispersion of those powders to then cover the electrode. Dr. Christian Durante & coworker explains to us how to use the SONICA Ultrasonic cleaner with Sweep System Technology to prepare a homogeneous dispersion of powder and compare that to traditional stirring.

Preparation of powder catalyst inks in hydroalcoholic solutions using an ultrasonic bath (SONICA 3200 EP) for coating glassy carbon rotating disk electrodes for electrochemical measurements

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For the electrochemical characterization of carbonaceous catalysts, or more in general, of powder catalysts, it became crucial to find a method to form a thin and homogeneous layer onto a catalytically inert electrode, typically glass carbon. The most common technique is the preparation of a homogeneous dispersion, named ink, which is dropcasted on the surface of the electrode. Since the typical loading on the electrode spans from 100 to 1000 μg cm^{-2} and the area from 0.1 to 0.3 cm^2 the actual amount of catalysts will be a fraction of milligrams. It is therefore fundamental to have control over the concentration of the ink, and not less importantly, over its homogeneity, to produce reproducible coatings (mass and quality).

We focused on the comparison between an ink sonicated and one stirred for variable time. A solution was prepared with carbon powder, water, and an organic solvent in a weight ratio of ca. 32:3:1. Sonication could be performed by placing the ink into a vial and let float with a piece of foam rubber, or by clamping it and finding the sweet spot on the bath, as shown in Figure 1. Stirring is instead performed with a magnetic bar inside the vial.

Figure 1. The SONICA 3200 EP used in this study.

Figure 2a at time zero and Figure 2b show the appearance of ink before starting; it is clear the separation of the solvent and solid. After only 5 minutes it is possible to observe (Figure 2a) that the ultrasonicated solution starts to homogenize, while the stirred one is still grainy and separated. After 90 minutes, even if the two solutions appear similar (Figure 2c) it is still possible to observe a better dispersion on the sonicated one. The huge advantage is seen after only 5 minutes of rest after the mixing, indeed the stirred solution starts to separate, while the sonicated one is stable (Figure 3). After 1 hour the stirred solution is separated like the starting point, while the sonicated one is still stable and homogeneous, the same is true after 1 day. It is important to stress that this is the major advantage of sonication, indeed having a homogeneous and stable ink, namely with the same powder content of catalysts across all volumes, guarantees to withdrawal of the same mass of catalysts in the subsequent casting of the electrodes.

Ultrasonic cleaning uses cavitation micro-to-nano-sized bubbles induced by high-frequency pressure (sound) waves to agitate a liquid. Stimulation induces a high force that can break down the agglomerate of powder that generally hinder the dispersion into the solution. Ultrasonication is indeed also less aggressive compared to probe sonicator, representing a good balance, in particular in the presence of nanoparticles grown on carbon, which can cause ultrasound-induced ablation, agglomeration, and dissolution of nanoparticles (*B.G. Pollet, J.T.E. Goh / Electrochimica Acta 128 (2014) 292–303)*. Finally, ultrasonic baths also allow for better control of the temperature of the ink, which is also a crucial parameter that can damage the catalysts.

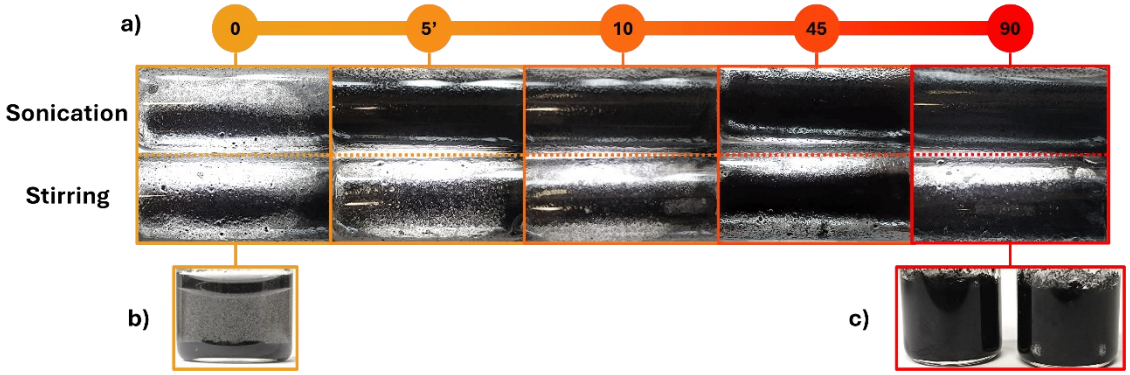

Figure 2. a) Photographical comparison between the same ink formulation after 5, 10, 45, and 90 minutes of sonication and stirring. b) starting solution. c) Final solutions. It is clear how the stirred solution is less homogeneous, even after 90' the result is worse than 5' in the ultrasonicator bath, in particular the stability, as shown in Figure 3.

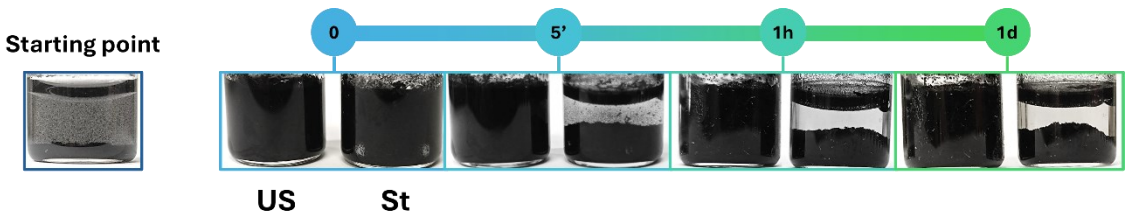

Figure 3. Photographical comparison of the stability of two inks. Stirred one is separating after only five minutes, the other is stable after 1d. The two solutions are reported in the order ultrasonicated (US) and stirred (St).

The quality of the ink, as said, impacts the control of the catalyst mass on the electrode and its homogeneity. By drop-casting the same amount of catalyst (0.6 mg cm^{-2}) onto a glassy carbon electrode, a difference was noticed in terms of the quality of the layer and recorded activity against the oxygen reduction reaction. The layer obtained by stirring (St in Figure 4, black) is not uniform and presents some agglomeration, less evident in the other layer (US in Figure 4, red). This is reflected in a lower limiting current for oxygen reduction in a rotating disk electrode setup (Figure 4). Since the activity (onset potential) is not different for the two electrodic layers, this could be caused by agglomeration and therefore lower exposure of the active site, which became more evident in the limiting current region.

So finally, we stress again, as proved by Figures 2, 3, and 4, how important is to produce a homogeneous ink to control the reproducibility of electrode preparation and therefore the reliability of the recorded electrochemical response; the SONICA 3200 EP easily allows to obtain the quality of the expected ink.

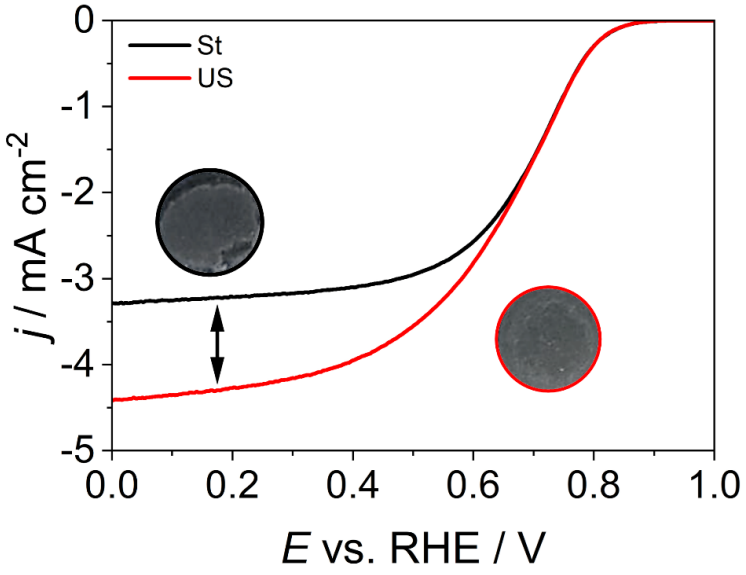

Figure 4. Image of the two catalyst layers obtained by drop casting and their response against oxygen reduction reaction in acid media (linear sweep voltammetry in O_2-saturated 0.5 M H_2SO_4, 1600 rpm, 5 mV s^{-1}, loading 0.6 mg cm^{-2}). St = stirred, US = ultrasonic.

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