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Atomically precise Pt-CO clusters for oxygen reduction reaction

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Global warming and the huge production of the greenhouse gases are very actual concerns. A new paradigm for energy production must be proposed, and in this context also the possibility to reduce the dependence on fossil fuel should be pursued. To date different solution are adopted: lithium storage, flywheels, water basins and H_2 production and storage. Also metal-air batteries have been largely investigated, in recent years, as possible very attractive alternatives as energy source/storage, especially for their low environmental impact and versatility: low cost, low emissions, light weight, and relatively high specific capacity and energy density. When chemical energy is converted to electrical energy in these devices, at cathode the Oxygen Reduction Reaction (ORR) must occur at as low as possible overpotential. This ask for a strong improvement of the ORR sluggish kinetics, about 5 orders of magnitude slower than hydrogen reaction, reducing, at the same time, the use of platinum and/or Platinum Group Metals as cathode material. In this context, Pt complexes, chosen in order to minimize the metal loading tough maintaining the same performance in term of specific activity, $mA \cdot cm^{-2}$, and mass activity, $mA \cdot g^{-1}$, as possible cathode material must be investigated. In this work, molecular metal clusters (MMC) based on Pt-CO complexes, with different CO/metal ratios, are synthetized and electrochemical characterized for ORR in alkaline media. These complexes date back to Chini compounds [1], already studied via electrochemical measurements in aprotic organic solvent to discuss their oxidation state and stability, and correlation between spectroscopic CO behaviour and electrochemical induce modifications [2]. Moreover, very recently, the carbonyl chemical route has been largely used to prepare very active electrocatalysts, due to the possibility of tailoring the surface electrode chemical composition and the shape and size of the nanoparticles [3]. In any case, the carbonyl moieties have been used to both control the metallic nanoparticles size and shape, in order to mix them with other metal particles to prepare bimetallic electrocatalysts, and fix them on a suitable carbon support. The research outcomes are discussed in term of electrochemical activity, stability and durability of the prepared cathodes.

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[2] Roth, J. D. *et al.* Exploration of the ionizable metal cluster-electrode surface analogy: infrared spectroelectrochemistry of [Pt24(CO)30]N, [Pt26(CO)32]N, and [Pt38(CO)44]N (n = 0 to -10) and comparisons with potential-dependent spectra of carbon monoxide adlayers on platin. *J. Am. Chem. Soc.* **114**, 6159–6169 (1992).
[3] Gago, A. S., Habrioux, A. & Alonso-Vante, N. Tailoring nanostructured catalysts for electrochemical energy conversion systems. *Nanotechnol. Rev.* **1**, (2012).