

Supporting information

Bipolar electrochemical milling for controlled size reduction of metal beads

J. Roche, E. Gianessi and A. Kuhn*

The home made cell used in this study is composed of a platinum mesh as feeder anode, a gold coated glass plate as feeder cathode and a perforated plastic cylinder as separator between the reaction chamber and the feeder electrodes. This separator allows both the current to flow across the bead chamber and the metal cations to migrate and diffuse towards the feeder cathode where they can be subsequently reduced, while preventing the microspheres from entering in electrical contact with the feeder electrodes. A magnetic stirrer is used to create convection in the system in order to uniformly oxidize the rotating metal beads. In a typical experiment, the cell is filled with synthesis grade ethanol containing 5 mM of H_2SO_4 and 5 copper beads with an initial diameter of 1 mm (Goodfellow). Sulfuric acid is used both as electrolyte to allow current to flow and to increase the solubility of Cu^{2+} in order to avoid precipitation of $\text{Cu}(\text{OH})_2$. A high voltage generator is used to apply the electric field between the feeder electrodes (Heinzinger). As can be seen from equation 1 in the main manuscript, smaller particles require linearly higher electric fields. This general feature of bipolar electrochemistry can become a limiting factor for the application of the concept. We've so far demonstrated in previous publications that the modification of micrometer size particles by bipolar electrochemistry is possible and therefore it should be possible to apply also the presented milling process for smaller objects. However the experimental set-up becomes then more complicated as membranes have to be introduced into the set-up and also a cooling system due to an increase in heat production through the Joule effect.

During a typical experiment, steady state is never reached both from an ionic force point of view (solvent evaporation and refill, metal ion formation and reduction as well as proton reduction) and from a temperature point of view. Both phenomena definitely change gradually the electric field profile in the bulk when the experiment is carried out over dozens of hours. Therefore the experiment has been stopped precisely every 60 min, the weight of the beads has been measured and the electrolyte has been replaced so that the electric field profile during the whole electrolysis is more stable and reproducible.

More generally and as usual in the case of bipolar electrochemistry, the conductivity of the electrolyte surrounding the particles should be as low as possible in order to make sure that a maximum part of the current is going through the objects and not through the solution. For this reason the electrolyte concentration has to be kept as low as possible. In the present case it was necessary to add a certain amount of acid in order to avoid the formation of oxides and hydroxides during the oxidation process, but for cases where this is not a problem very small concentrations of electrolyte are recommended .