Electronic Supplementary Material (ESI) for Chemical Science

Supplementary information

Chemicals

All chemicals were used as received; solutions were prepared using Milli-Q water (resistivity = 18 MΩ cm) or absolute ethanol (Sigma Aldrich). Glassy carbon spherical beads (type 1, 200-400 μm) were supplied by Alfa-Aesar. Absolute ethanol, gold(III) chloride trihydrate (> 99 %), silver nitrate (>99%), ethyl cellulose (48% ethoxyl) and chloroplatinic acid (> 99.9 %) were purchased from Sigma-Aldrich. Nafion® membranes N424 were supplied by ion power.

Cell configuration for the modification of micrometer sized beads

The cell is composed of one reaction compartment, in which the substrates and the reagents are located, separated by two Nafion ® N424 membranes from the two electrode compartments. The feeder electrodes, which are immersed in cold ethanol containing no reactants or only supporting electrolyte, are connected to a high voltage power supply Heinzinger (PNC 30,000 – 20 ump). The distance between both feeder electrodes is 3.3 cm. Gold plates were used as electrodes.

200 μm - 400 μm carbon beads modification

An ethanol based gel was first prepared by dissolving ethyl cellulose in absolute ethanol at 200 g.L^{-1}. The mixture was then sonicated for at least an hour until a homogenous gel has been obtained. 30 mg of 200-400 μm glassy carbon beads, previously washed and sonicated in absolute ethanol, were then added to 6 ml of the ethyl cellulose gel. 0.25 mM H_2PtCl_6 or 0.25 mM of $HAuCl_4$ were added and the mixture was stirred until the beads were well dispersed. 4 ml of the resulting mixture were introduced into the reaction compartment of the cell. Ethanol, containing 1 mM of NH_4Cl as supporting electrolyte, was cooled for 1 min in liquid nitrogen and then added to the electrode compartments. For single ring particles, a voltage bias of 2.0 kV was imposed for 20 s. For parallel double ring particles a first run with a voltage bias of 2.0 kV was imposed for 10 s then a second run of opposite polarity was carried out for 10 s. For perpendicular double ring particles, the reaction compartment was turned by 90° between the two runs. After modification, the gel was taken out from the reaction compartment for the washing step.

Isolation and washing of carbon beads modified in ethyl cellulose gel matrix

The gel containing the modified beads was dissolved in 50 ml of absolute ethanol under stirring. The resulting solution was then centrifuged at 3000 rpm for 2 min. The supernatant was removed and this washing process was repeated 3 times. Finally, the modified beads were kept in a small volume of ethanol for conservation.

Simulation Software Comsol Multiphysics v3.4.

The description of the transport of matter is based on the Nernst-Planck equation. The mesh used consists of 9384 elements.

D	10^{-5} cm²s^{-1}	Diffusion coefficient
F	96485.3 C mol^{-1}	Faraday constant
n	1	Number of electrons
C_o^0	10^{-3} mol L^{-1}	Initial concentration of oxidized species
C_r^0	0 mol L^{-1}	Initial concentration of reduced species
E_0	0 V	Standard potential
R	8.314472 J mol^{-1} K^{-1}	Gaz constant
T	298 K	Temperature
K_e	5 10^7 S m^{-1}	Bipolar electrode conductivity
K_s	7.5 10^{-3} S m^{-1}	Solution conductivity
k_0	0.1 m s^{-1}	Standard rate constant
α	0.5	Charge transfer coefficient

Table 1: Constants used for the simulation.

Electron transfer, at the bipolar electrode boundary, is described with the Butler-Volmer formalism, which is used to evaluate the flux of species consumed and generated at the bipolar electrode.

$$-D_O \nabla C_O + \frac{F}{RT} D_O C_O \nabla \phi = -k^0 \exp\left(-\alpha \frac{F}{RT}\left(E - E^0\right)\right) C_O + k^0 \exp\left(\left(1-\alpha\right)\frac{F}{RT}\left(E - E^0\right)\right) C_O$$

$$-D_R \nabla C_R = k^0 \exp\left(-\alpha \frac{F}{RT}\left(E - E^0\right)\right) C_O - k^0 \exp\left(\left(1-\alpha\right)\frac{F}{RT}\left(E - E^0\right)\right) C_R$$

The geometry of the simulation space is depicted in Figure S1 (drawing not to scale), the bead (diameter l = 1 mm) is at equal distance from the two feeder electrodes. The inter-electrode distance is d = 2 cm and the distance between bottom and top of the cell h = 8 mm.

The bulk concentration values are used to represent the semi-infinite boundary condition for type *i*, *ii* and *iv* boundaries. The inward flux at boundary *iii* is described by Butler-Volmer formalism. Potential at the boundary *ii* is E and –E at the boundary *iv*. The potential starts at 0 V and is changed as a function of time during the first 10 s, the rate is 1 V/s. For t > 10 s E is kept at the constant value of 10 V.

We made the approximation that no faradic reaction occurs at the cathodic and anodic feeder electrodes (boundaries *ii* and *iv*), which reflects the fact that membranes are used between the electrode compartments and the reaction compartment in order to avoid that the faradic reactions at the electrodes disturb the reactions at the bipolar electrode. The boundary i is insulating.

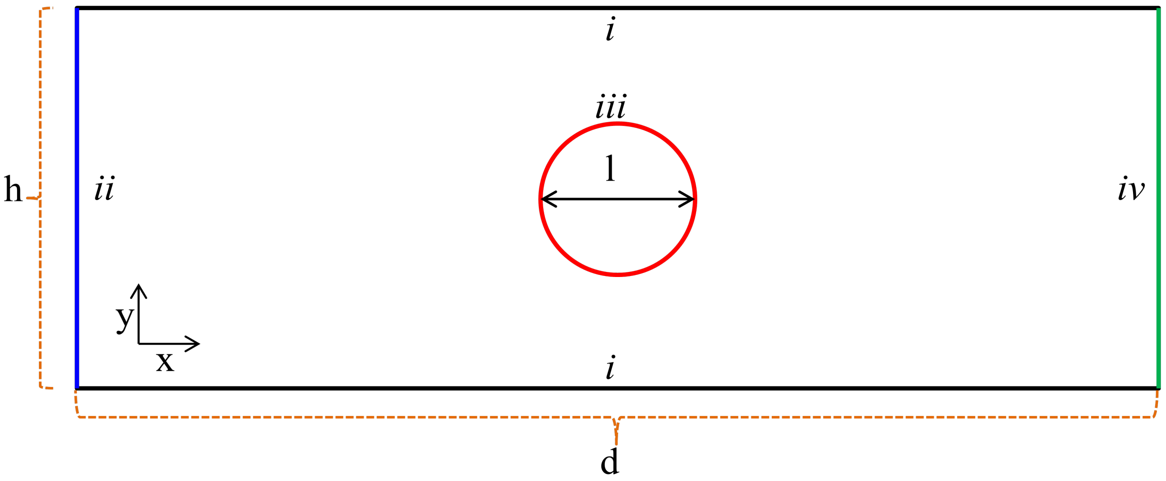

Figure S1. Scheme of the geometry used for the simulation of the concentration profile of species generated at the bipolar electrode. All geometries are in axial 2D and described by x and y. Boundary types: i, insulator; ii and iv bulk concentration (semi-infinite); iii, flux at the bipolar electrode. The length of the cell was d *= 20 mm, the bead's diameter was* l *= 1 mm. Scheme not at scale.*