

The Silver Electrocrystallization onto Carbon Electrodes with Different Surface Morphology: Active Sites vs. Surface Features

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This study is dealing with a silver electrocrystallization process onto carbon electrode substrate, as the earliest stage of the silver bulk deposition. The deposition was carried out from 10^{-2} M $\text{Ag}(\text{NH}_3)_2^+$ /1.6 M NH_3 , 1 M KNO_3 (pH=11) electrolyte solution, on three rather typical carbon electrodes: HOPG, MPVC and FVC. As verified by AFM imaging, just before the silver deposition process, each of the used electrodes possesses its own and characteristic surface morphology. Indeed, the AFM images revealed details of the surface structure, shape and size of typical surface features and surface roughness (via RMS[Rq] factor), which were the base for qualitative and quantitative evaluation of the electrode surface morphology.

The main aim of our study was to determine a possible influence and establish a relation between the carbon electrode surface morphology and the course of the silver electrocrystallization process. It is a topic of a special interest since electrocrystallization process exclusively proceeds via deposition active centers and deposit nuclei formation mechanism, which could not necessarily be the function of macroscopic characteristic of the electrode surface.

The electrochemical techniques: cyclic voltammetry and chronoamperometry have been used to study the silver electrocrystallization process. Cyclic voltammetry offers a more general type of parameters helpful to characterize position (potential) of the silver deposition/dissolution peaks, total charge related to deposition and silver dissolution process. Interestingly, silver deposition/dissolution peaks were always found on the same potentials regardless the carbon substrate used. However, the total amount of charge related to silver deposition or dissolution process was found to have direct relation to the electrode surface roughness (RMS[Rq] factor). The trend among the obtained data is very clear, more charge, which could also be extrapolated to more silver deposit, is associated with carbon surface with higher surface roughness. Thus, the silver deposition efficiency was found to be the highest on FVC electrode (the highest surface roughness), and decreases for MPVC to HOPG (the lowest efficiency and the lowest surface roughness). The simplest explanation seems to be a relation between silver deposition efficiency and the electrode active area (increase due to the surface roughness). However, as our analysis shows, the relation is not straightforward (linear), and increase in the electrode surface roughness is not proportionally followed by increase in the deposition charge (silver deposit), which is clearly indicating that beside surface morphology other factors must have influence on the electrocrystallization process, too.

In order to obtain more specific information about the silver electrocrystallization process, in particular, as for the characteristics related to electrode surface conditions and mechanism of surface processes, a chronoamperometric study was performed. The research was based on current-transient measurements, their analysis and evaluation of characteristic kinetic parameters for silver electrocrystallization (nucleation and growth) process. Detailed analysis of the recorded current transients and their comparisons with adequate theoretical models clearly indicate that on all three carbon substrates, silver deposition can be classified as 3D electrocrystallization process controlled by silver ions diffusion kinetic. However, the process takes place in different potential ranges in dependence on the substrate used (or the substrate surface characteristics). The amount of overpotential necessary to initiate 3D silver deposition reaction raises from HOPG, over FVC to MPVC electrode surface. We suppose that observed trends are related to electrode surface conditions, including surface morphology and the fact that MPVC electrode is most probably covered with some kind of oxide adlayer, as a result of polishing procedure.

On all three surfaces, at lower overpotentials, current transients are closer to progressive type, but the increase in overpotential leads to shift to instantaneous type. Further analysis of kinetic parameters of silver deposition process involved estimation of: nucleation rate (A), number density of active sites (No), saturation number density of the formed silver nuclei (Ns) and charge during the first 20 s of potentiostatic transients of the silver electrocrystallization process (Q). Although there are parameters which define kinetics of silver deposition process, their sensitivity to electrode surface conditions make them useful in the evaluation of the electrode surface quality.

Beside some expected and rather regular behavior of such A, No, Ns, and Q at with overpotential, found for all three substrates, we also found that HOPG possesses higher number of No and charge density Q. The minimum No was recorded on the MPVC electrode. However, density of formed silver nuclei was found to be the highest on the FVC substrate, and gradually drops to lower value on HOPG and MPVC, respectively. The Ns/No ratio (efficiency of active sites use) was found to be the highest on MPVC substrate. Thus HOPG possesses the highest active sites number, but does not use all of them so efficiently as they are employed on MPVC substrate. Charge consume per a formed silver nuclei also appears as very interesting parameters. The smallest charge transfer was found to be associated with formation of silver nuclei on the FVC electrode substrate. As a final aim we attempted to relate the difference among kinetic parameters obtained on different substrates to the quality and conditions on the carbon electrode surface (i.e. surface roughness factor). Our results clearly show lack of a straight and simple relation, which could connect such two sets of parameters. Electrocrystallization process seems to be very specific reaction which proceeds over a very small portion of the electrode surface, in and around active sites zones, which possibly have very specific characteristics in the sense of the surface structure and electronic properties. Therefore, macroscopic parameters like, surface roughness, number of surface features and surface morphology characteristics, visualized by AFM images, do not really have relation with such surface limited process. As discussed in the last part of paper, further progress and better understanding of a metal electrocrystallization process on foreign substrates is limited by poor understanding of the active site meaning and low possibility for their visualization by the microscopic techniques.

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