Chemical "Kick Start" for the Autocatalytic Formaldehyde-Free Electroless Copper Plating Process

Edith Steinhäuser
Dr. Lutz Stamp
Dr. Lutz Brandt
Tafadzwa Magaya
Atotech Deutschland GmbH, BTT PTH

Abstract

The present work describes the use of additives in formaldehyde-free copper solutions to improve the start reaction of electroless copper deposition.

Conventional electroless copper plating solutions contain a copper salt, one or several complexing agents, a reducing agent, a pH adjusting agent as well as stabilizers and other additives.

At the present time formaldehyde is the established reducing agent in electroless copper metallization of plated through-holes. Because of its environmental impact, there is a need to replace formaldehyde. Many alternatives have been suggested but some of them pose a greater health and safety threat than formaldehyde does and some alternatives are not economically viable.

In this investigation, the more environmentally friendly glyoxylic acid is used as an autocatalytic reducing agent. However glyoxylic acid is more expensive and causes undesirable side reactions. Consequently, it leads to a rise in the price of the copper plating process. In order to keep process costs under control, the concentration of glyoxylic acid in the copper bath should be reduced without affecting the quality of the copper deposits.

Therefore, additives are introduced which can compensate for the lower reducing agent concentration, and thus the lack of essential electrons for the copper deposition.

On palladium-activated base material, the additives react with the palladium and generate additional electrons in the initial phase of the deposition. Thus, the adequate supply of electrons from two sources permits the deposition of a homogeneous and compact copper layer.

Keywords

Electroless copper, formaldehyde-free, glyoxylic acid, startup agents, palladium-activated

Introduction

Electroless copper plating is widely used for the fabrication of printed circuit boards and other electronic devices. The manufacture of printed circuit boards is an established technology, encompassing low cost and high yield whilst maintaining a high quality deposit. Conventional electroless copper plating solutions contain a copper salt for the delivery of the copper ions, one or several complexing agents for the copper ions, a copper ion reducing agent (usually formaldehyde), a pH adjusting agent as well as stabilizers and other additives.

In the process of electroless copper deposition, it is necessary to activate the surface of a non-conductive dielectric with palladium. The catalytic palladium deposit is used to overcome the kinetic barrier of electroless copper deposition. The electroless copper plating process is initiated on the randomly distributed catalyst seeds on the substrate. This mechanism facilitates communication between electrical components and related conductors [1].

The use of reducing agents in the electroless copper baths is necessary for achieving an autocatalytic plating process. Various common reducing agents, especially formaldehyde, lead to environmental and health hazards. Other alternative reducing agents are very expensive. In addition, high reducing agent concentrations can cause undesirable side reactions in the copper solution.

In this study the environmentally friendly glyoxylic acid is used as an autocatalytic reducing agent. It has the disadvantage however that it is more expensive than formaldehyde. Furthermore, by-products in working solutions containing glyoxylic acid are built up rapidly and lead to a short solution life time.

Therefore, the aim is to reduce the disadvantageous qualities of the autocatalytic reducing agent without affecting the quality of the copper deposits. This can be achieved with a low reducing agent concentration in the copper solution. To compensate for the resulting lack of reducing agent, and thus the lack of essential electrons for the copper deposition, additives are introduced. These additives support the startup process on palladium-activated base material during the copper deposition. The additional compounds operate only on the palladium and are not developed as a substitute for the traditional copper reducing agent. The reducing agent is still a fundamental requirement. A minimum amount of reducing agent is necessary for the autocatalytic copper plating process.

This investigation demonstrates that additives can provide a significant benefit in terms of cost because a higher concentration of the cost-intensive reducing agent can be avoided.

1 Reaction mechanism

The surfaces of epoxy resin substrates are easily metalized by the electroless copper plating technique. The basic bath composition was

Cu (as $CuSO_4$)	0.03 mol/l
HEDTA	0.036 mol/l
CHOCOOH	0.018 – 0.073 mol/l
Additive	0 – 0.15 mol/l
Stabilizers	ppm range
Temperature	50 °C
pH	12.8

Electroless copper deposition reactions at palladium-catalyst-adsorbed surfaces consist of two partial reactions. At the anodic surface, the reducing agent is oxidized and at the cathodic surface, copper ions are reduced to a metallic state.

Oxidation of the autocatalytic reducing agent glyoxylic acid:

$$CHOCOOH + 2OH^- \rightarrow (COOH)_2 + H_2O + 2e^- \quad <1>$$

Reduction of cupric ions:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad <2>$$

Both reactions occur simultaneously at the surface of the palladium catalyst. The release of electrons is necessary for the copper reduction. Through the oxidation of the reducing agent, electrons are delivered and used for the autocatalytic copper plating process.

In order to lower the disadvantageous qualities of the reducing agent, its concentration in the copper solution must be decreased. However, lower reducing agent concentrations yield fewer electrons. The insufficient amount of electrons leads to an inhomogeneous and scant copper deposition. Therefore, in order to produce high-quality copper coatings with low reducing agent concentration, additional electrons must be provided.

2 Electrolyte additives

The supply of electrons for electroless copper deposition can be increased by using electrolyte additives, which are able to discharge additional electrons. At the beginning of the chemical copper plating process, a sufficient supply of electrons is important for creating a defect-free and uniform copper deposition even at low concentrations of the autocatalytic reducing agent. If the initial deposition is locally inhibited, inhomogeneous deposits will be formed irreversibly. For a perfect and defect-free startup process of the electroless copper deposition on palladium-adsorbed surfaces, additives can be used which react with palladium. The following additives, the use of which has been reported [5], were investigated: sodium hypophosphite, glycolic acid and sodium formate.

Additional electrons are delivered by exploitation of the catalytic qualities of palladium. The electrons develop during the oxidation reaction of the electrolyte additives on the palladium seeds:
Additive oxidation (additive 1: $H_2PO_2^-$):

$$H_2PO_2^- + 3OH^- \xrightarrow{\textbf{Pd}} HPO_3^{2-} + 2H_2O + 2e^- \quad <3>$$

By use of such additives an accelerated copper deposition can be achieved. The deposition rate increases with additive concentration and amount of adsorbed palladium on the surface. This can be explained by the release of additional electrons, which can be used for the copper reduction. The catalytic qualities of palladium allow it to act as a charge ex-

changer. It carries the electrons delivered from the additive oxidation process to the cupric ions to reduce them to metallic copper. The amplified supply of electrons leads to an enhanced copper reduction.
The maximum of deposition speed in copper solutions with an additive occurs in the initial phase of the electroless copper deposition. This peak is clearly greater than the deposition speed maximum in electrolytes without an additive (*Figure 1*).

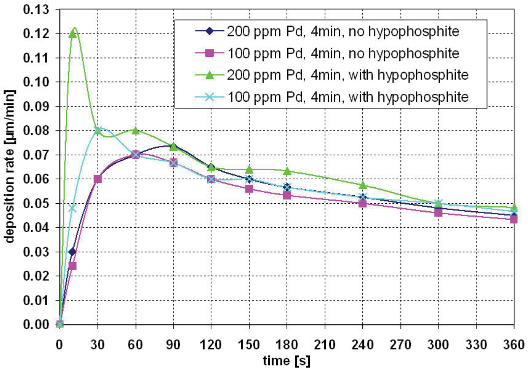

Fig. 1: Comparison of the deposition rate in copper solutions with/ without hypophosphite

Decreasing the palladium adsorption on the surface reduces the rate of copper deposition (*Figure 1, comparison between green and light blue curve*).

The use of sodium hypophosphite in the copper bath stimulates a maximum deposition rate within 30 seconds. Although a maximum deposition rate is also achieved without the additive, its onset occurs about a minute later and it is less pronounced.

The maximum in the curve originates from the change in copper deposition, which first takes place at the catalytically active palladium seeds and then continues on the chemically deposited copper (*Figure 1, violet and dark-blue curve*).
The oxidation of the autocatalytic reducing agent is more extensive on the palladium than on the chemically deposited copper.

Palladium is a better catalyst for the copper reduction than the copper itself. Thus the deposition rate decreases when all of the palladium has been covered with copper.

The curves of the electroless copper solution with and without the sodium hypophosphite enhancement become nearly identical after a plating time of 90 seconds. After that time, hypophosphite has no more influence on the electroless copper plating process.

In general, one can assume that a maximum deposition rate is achieved when a maximum activation and exposure of the palladium is present. The use of an electrolyte additive (e.g. sodium hypophosphite) in conjunction with a large amount of homogeneously-distributed palladium seeds on the surface can further enhance the deposition performance.
The additives could be referred to as startup agents because they only react in the initial phase of the electroless copper deposition. At the beginning of the chemical plating process palladium seeds are active and affect the additive oxidation. The raised supply of electrons can subsequently induce an accelerated deposition.

The additives are effective at raising the initial plating reactivity via a catalyst metal. Since deposition uniformity at the start of the plating process is higher, the copper deposit homogeneity on the whole activated base material is enhanced (*Figure 2*).

Fig. 2: Initial phase of the electroless copper plating process on palladium-activated basic material without addition of hypophosphite (on the left) and with hypophosphite (on the right)

Already after 1 minute of the copper plating process there is a clear difference in the copper distribution of the material. Although the concentration of the reducing agent in the copper solution is very low (c < 0.05 mol/l), the copper deposition on the substrate is improved by the addition of hypophosphite (*Figure 2 right*). Without using the additive and with a low concentration of reducing agent, the copper deposition is neither sufficient nor homogenous (*Figure 2 left*).

Similarly, the copper deposition quality is improved on the surface as well as in mechanically created physical structures (e.g. drilled holes in the printed circuit board, *Figure 3*).

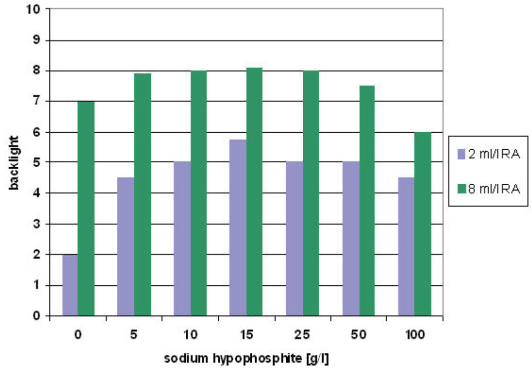

Fig. 3: Variation of the hypophosphite concentration and its effect on the drilled hole covering (backlight, 1: poor, 10: excellent) with different amounts of reducing agent (RA)

The comparison between low and high reducing agent concentrations (2 ml/l and 8 ml/l) shows that the effect of the additive (hypophosphite) is substantially stronger if the reducing agent concentration is kept low.

In the cases in which electrolytes with 2ml/l reducing agent concentration were used, the degree of copper coverage in the drilled holes more than doubles as the amount of hypophosphite is increased from 0 g/l to 15 g/l.

Beside sodium hypophosphite, the copper deposition is also improved by using glycolic acid or sodium formate as “kick-starting” agents. The copper deposition speed and the homogeneity of the copper coverage improve.

3 Conclusions

In the initial phase of the electroless copper deposition, the adsorbed palladium seeds formed by the activation process of the non-conductive substrate serve as an anode for the oxidation of the reducing agent. The electrons that are supplied by the oxidation reaction cause the copper reduction.

In electroless copper solutions, the reducing agent is necessary to maintain the autocatalytic copper plating process. Formaldehyde-free electroless copper solutions containing glyoxylic acid as an alternative are more expensive due to the cost-intensive reducing agent.

If the concentration of the reducing agent is reduced in order to minimize disadvantageous qualities and side-reactions, the amount of delivered electrons by the oxidation of the reducing agent is not sufficient to generate a compact copper layer. Therefore, a high degree of copper coverage of the layer can not be achieved, especially at the beginning of the plating process. This leads to an inhomogeneous copper deposition.

By the additional use of a chemical substance (electrolyte additive), which can be easily oxidized at a palladium surface, more electrons can be created. The electrons originate from the oxidation reaction of the autocatalytic copper reducing agent as well as from the oxidation reaction of the electrolyte additive. The electrons are generated in amounts sufficient for the deposition of a homogeneous and compact copper layer.

Suitable additives are sodium hypophosphite, glycolic acid and sodium formate. They can be oxidized at catalytically active palladium seeds and provide additional electrons for the electroless copper deposition. However, the additives are not reducing agents for the autocatalytic copper plating process. The autocatalytic reducing agent glyoxylic acid must be present in the copper solution and cannot be substituted completely.

The additives react exclusively with palladium. Therefore, they can be considered as a sort of startup agent for the copper plating process on palladium-activated base material. Palladium works by its catalytic qualities as an electron carrier.
In the course of the copper plating process, the palladium seeds are covered with copper after a short time and are no longer catalytically active. Then, the supporting effect of the electrolyte additives ceases. Without palladium, additional electrons cannot be generated and the autocatalytic copper deposition goes on steadily only because of the presence of the reducing agent in the electrolyte.

The use of additives to provide a chemical kick start may provide the following benefits:

- Lower health risks
- Lower costs due to non-process-relevant side reactions (e.g. Cannizzaro effect)
- A better quality of copper deposition.

By enhancing the plating reactivity in the initial phase, plating with lower concentrations of the reducing agent is realized.

4 References

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[5] Chowdhury; Electroless Plating Baths for High Aspect Features; US 7220296 B1; 2007

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Edith Steinhäuser, Atotech Deutschland GmbH
Email: edith.steinhaeuser@atotech.com

Presentation structure

1. Introduction

2. Reaction mechanism

3. Electrolyte additives
   3.1 Supporting effect

   3.2 Electrochemical characterization

4. Conclusions

1. Introduction

1 Introduction

Electroless copper plating solutions

- Copper salt
- Complexing agents
- Copper ion reducing agent
- pH adjusting agent
- Stabilizers
- Additives

Plating Process

- Pretreatment
- Main Step

Process Sequence –
Pretreatment (Cleaning, Conditioning and Etching)

Cleaner

Conditioner

Etch cleaner

Cleaning

→ Clean the surface of organic residues, like fingerprints, etc.

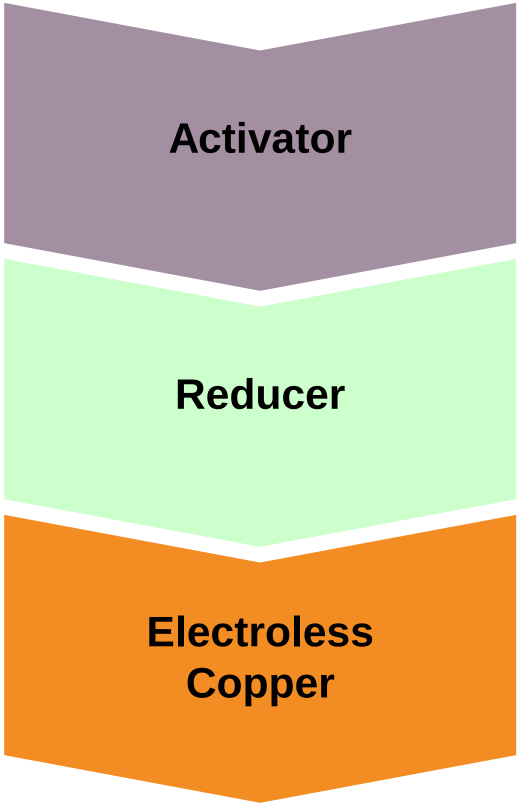
Conditioning

→ Prepare the base material, especially the glass fibres for the following activation process. Necessary, if desmear process is not Atotech or for special base material

Etch cleaning

→ Removal of copper oxides and micro roughening of the copper surface

Process Sequence –
Main Step (Activation, Reducing, Coverage)


Activator

Reducer

Electroless Copper

Activation
→ Adsorption of palladium ions on the conditioned surfaces.

Reduction
→ Palladium ions reduced to metallic palladium seeds.

Electroless Copper
→ Palladium-initiated auto-catalytic electroless copper deposition

One critical point: Reducing agent

- ➢ Essential
- ➢ Environmental and health hazards
- ➢ Cost efficiency
- ➢ Side reactions

Aim: Reducing the disadvantageous and harmful properties

→ Without affecting the quality

→ Reducing agent concentration ↓

→ Compensation by using additives

2. Reaction Mechanism

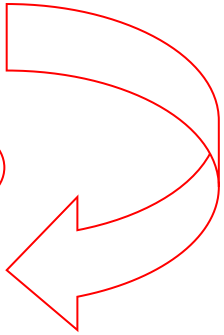
2 Reaction mechanism

Main reaction: Redox reaction

→ Anodic reaction: $HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^-$

or

$CHOCOOH + 2OH^- \rightarrow (COOH)_2 + H_2O + 2e^-$



→ Cathodic reaction: $Cu^{2+} + 2e^- \rightarrow Cu^0$

$[Cu\text{-}L]^{2-} + 2e^- \rightarrow Cu^0 + L^{4-}$

Side reactions

→ Cannizzaro

→ Carbonization

3. Electrolyte Additives

3 Electrolyte additives

- Disadvantageous qualities of the reducing agent ↓

⤷

Concentration of reducing agent↓

⤷

Electrons ↓

⤷

Inhomogeneous copper deposition → Quality of deposit ↓

⤷

Additional electrons → Quality of deposit ↑

3 Electrolyte additives

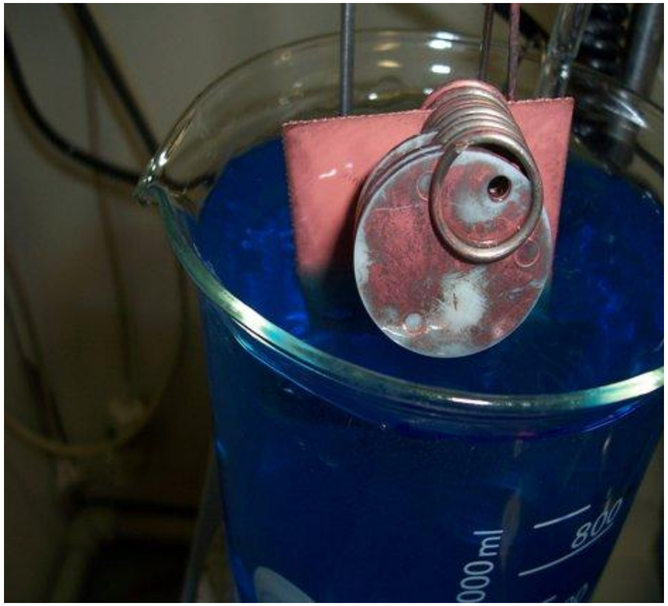
3.1 Supporting effect

3.1 Supporting effect

- Goal to decrease amount of reducing agent in order to minimize side reactions and improve cost efficiency → problem: low reducing agent concentration equals to poor copper deposition

- Need additive to improve bath performance

- Selection of additives from literature:
  - → **Three different additives**
  - Sodium hypophosphite
  - Glycolic acid
  - Sodium formate



- Additives are not reducing agents for the autocatalytic copper deposition

- React with the catalytic active palladium → only active on the palladium surface, not in the copper solution → oxidation process of the additive

$$\mathit{Additive}^{-} \overset{\mathbf{Pd}}{\rightleftharpoons} \mathit{OxAdditive} + \boxed{e^{-}}$$

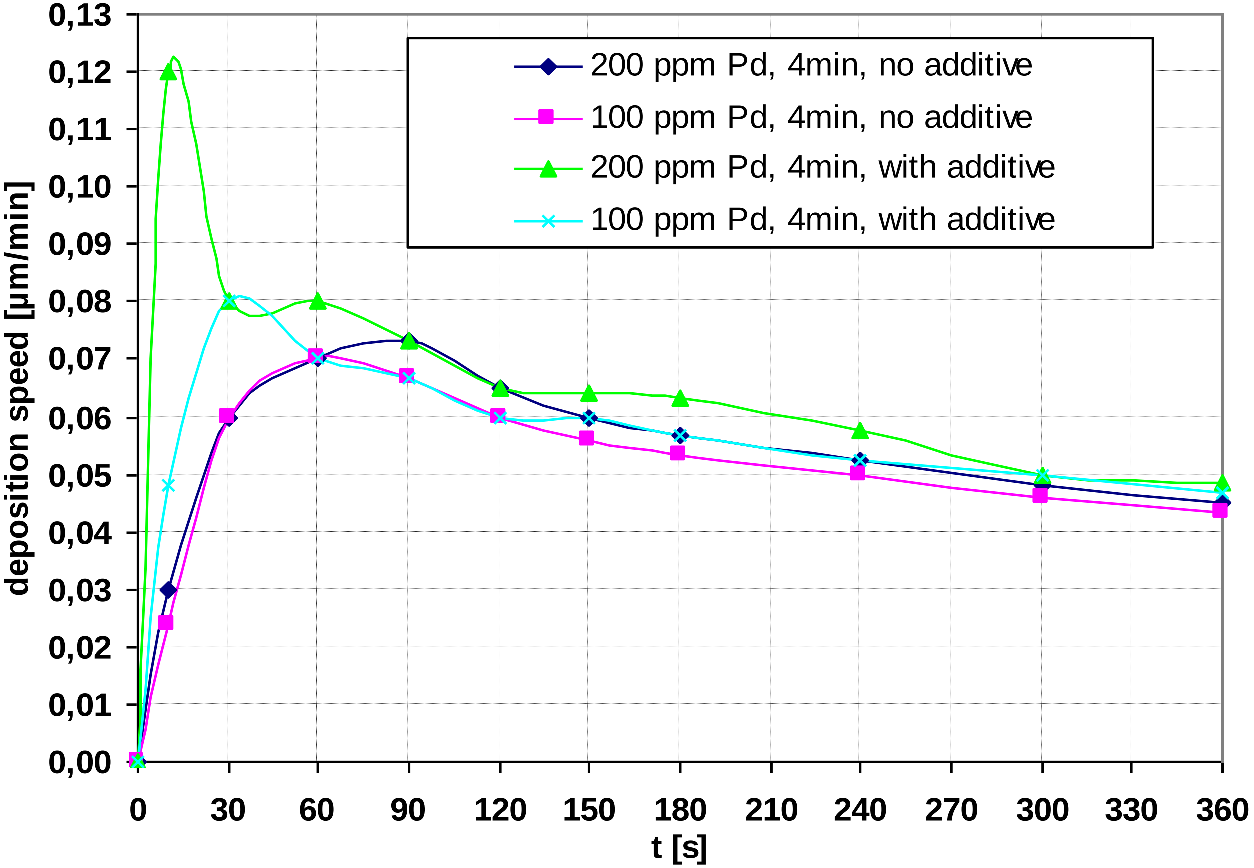
- Additional electron development → can be used for copper reduction

$$Cu^{2+} + \boxed{2e^{-}} \rightleftharpoons Cu$$

- Accelerate the copper deposition in the initial phase → additives can increase the deposition speed

- „Start up“ agents

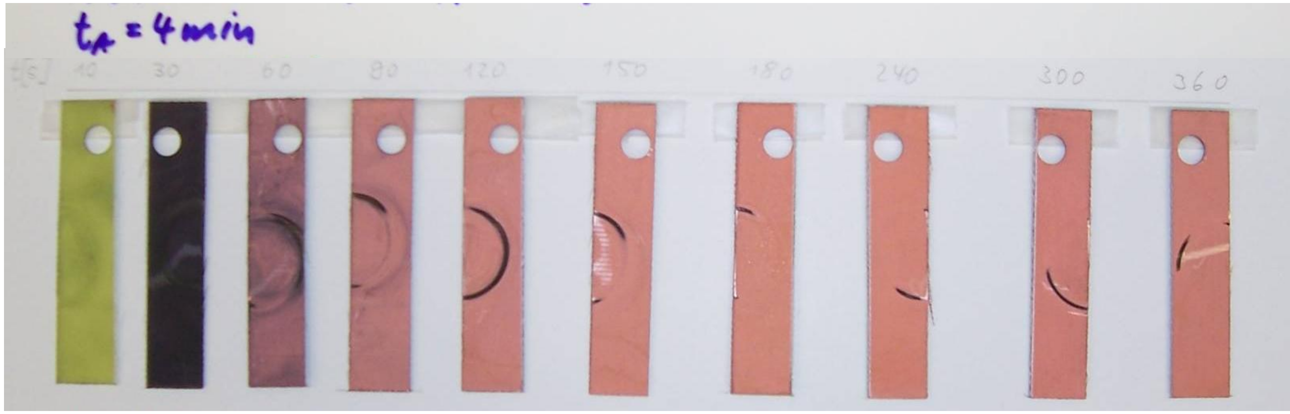
Acceleration of deposition speed at the beginning of plating:



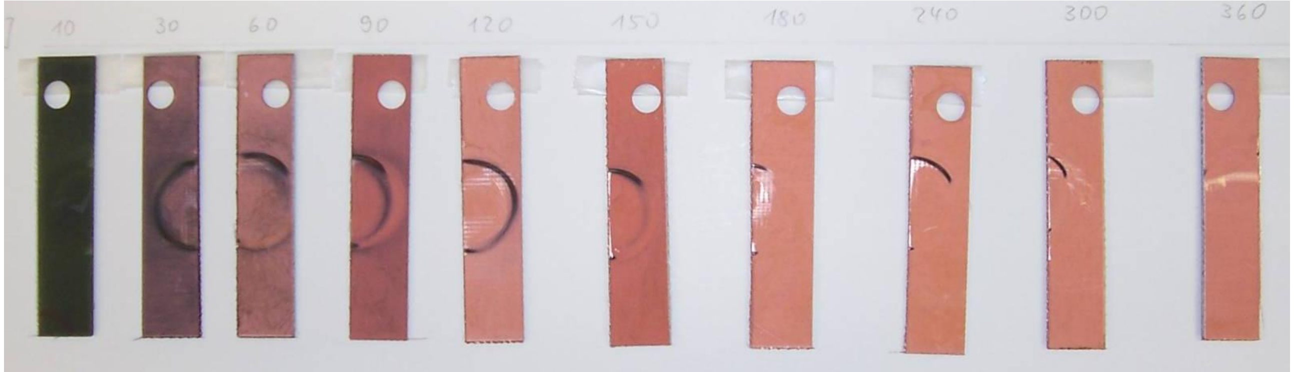
- Greatest effect in the first seconds of electroless copper deposition
- Maximum of deposition speed is influenced by palladium concentration

Influence at the initial phase:

- No additive and low concentration of reducing agent



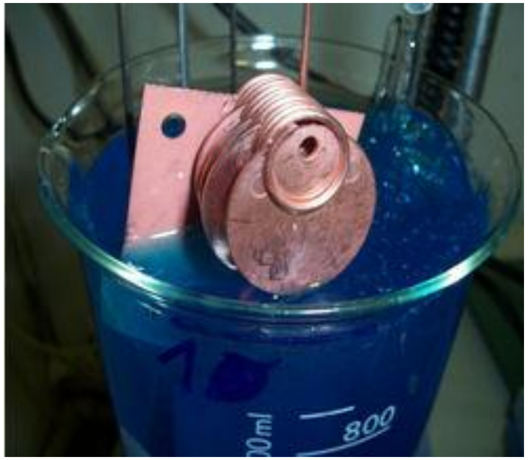
- Additive and low concentration of reducing agent



Improvement of copper coverage:

- Low concentration of reducing agent (c_{RA} = 0,036 – 0,072 mol/l)

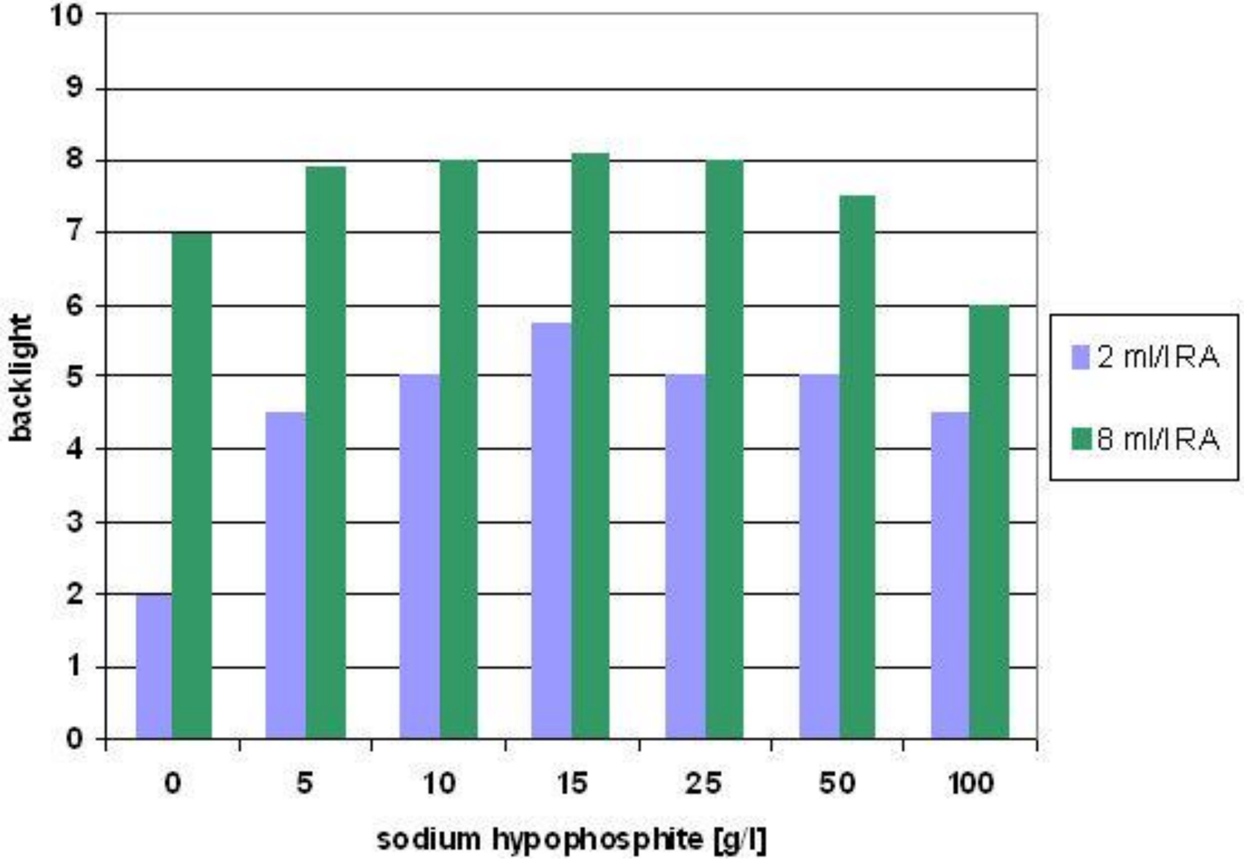
Without additive



With additive

- Because of additive oxidation process → more electrons for copper reduction
- Palladium has catalytic properties
- Additives cannot replace the autocatalytic reducing agent
- Support effect of additive ends when palladium is covered with electroless copper

Improvement of copper coverage:



3 Electrolyte additives

3.1 Supporting effect

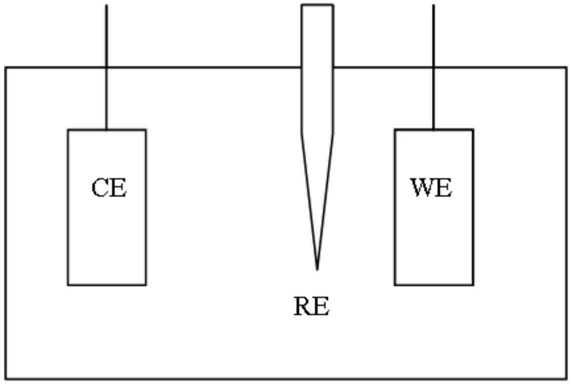
3.2 Electrochemical characterization

3.2 Electrochemical characterization

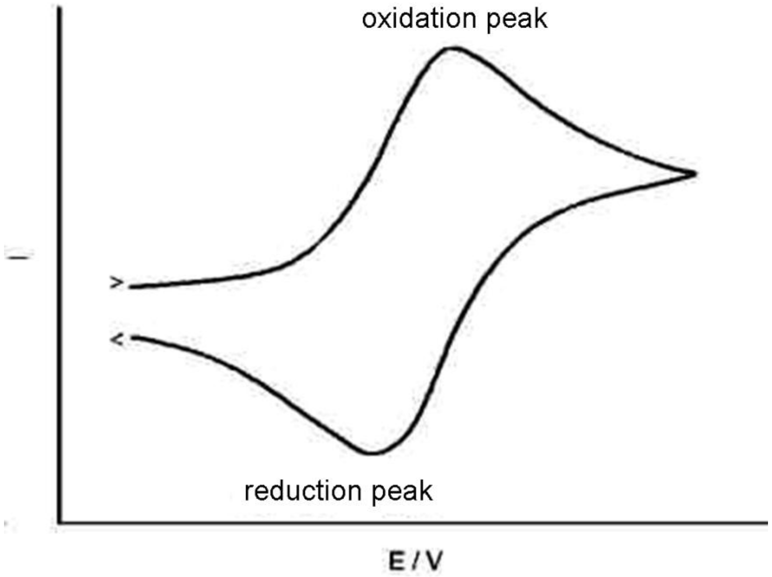
- Prove reaction of the additive

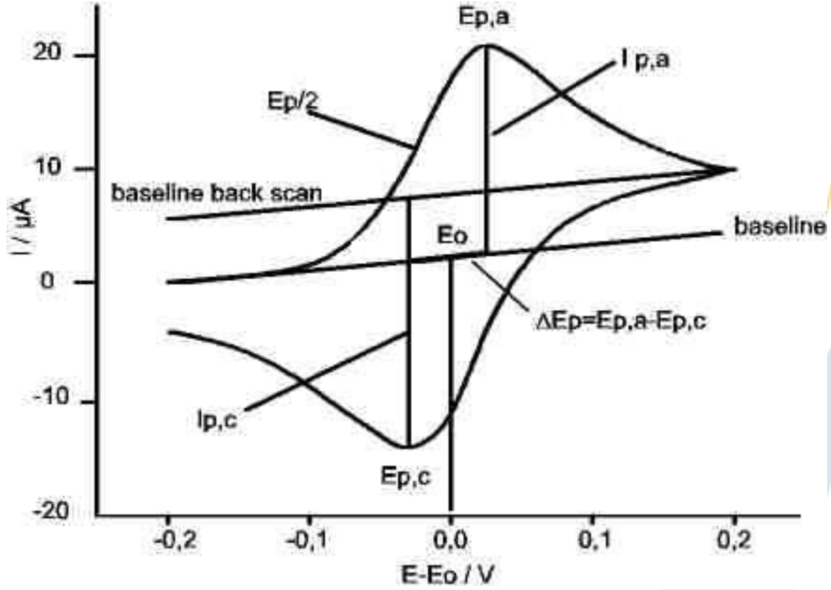
- Cyclic voltammetry

- RE: Ag/AgCl
- CE: Pt
- WE: Pd (Cu, Ni)

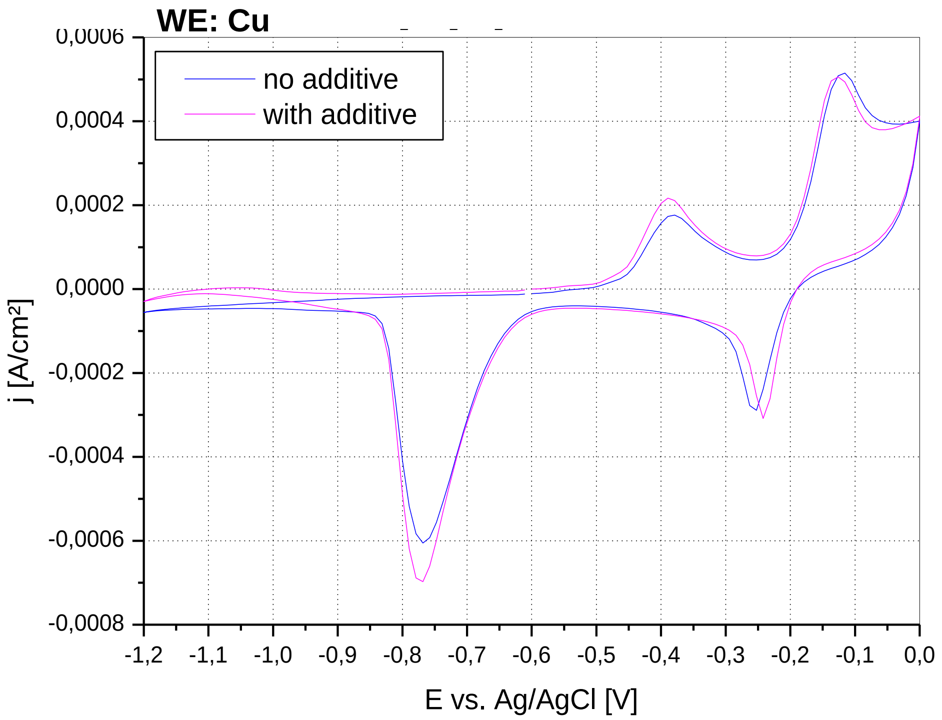


- Cyclic voltammogram

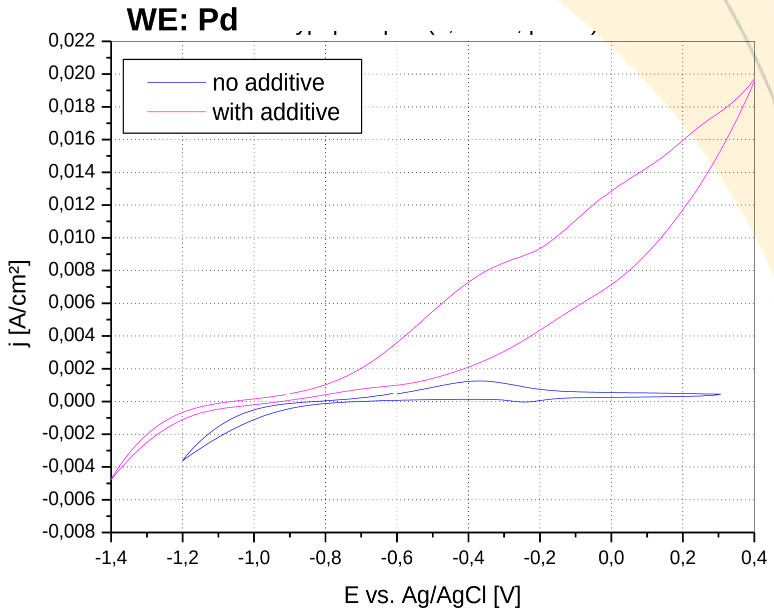




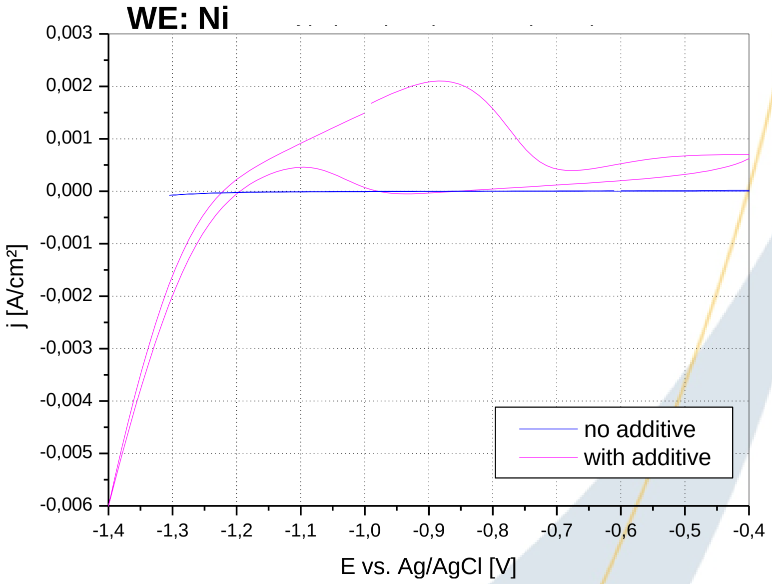
CV of NaH_2PO_2 at different working electrodes (WE) $c_{additive}$ = 0.3 mol/l; pH 13.0



WE: Cu



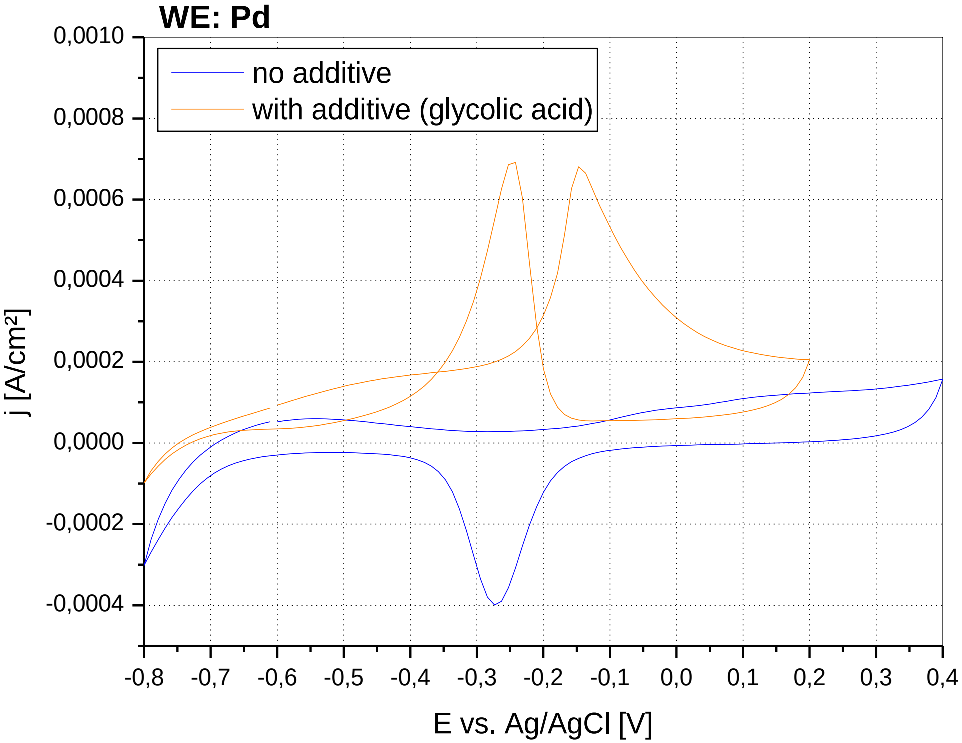
WE: Pd

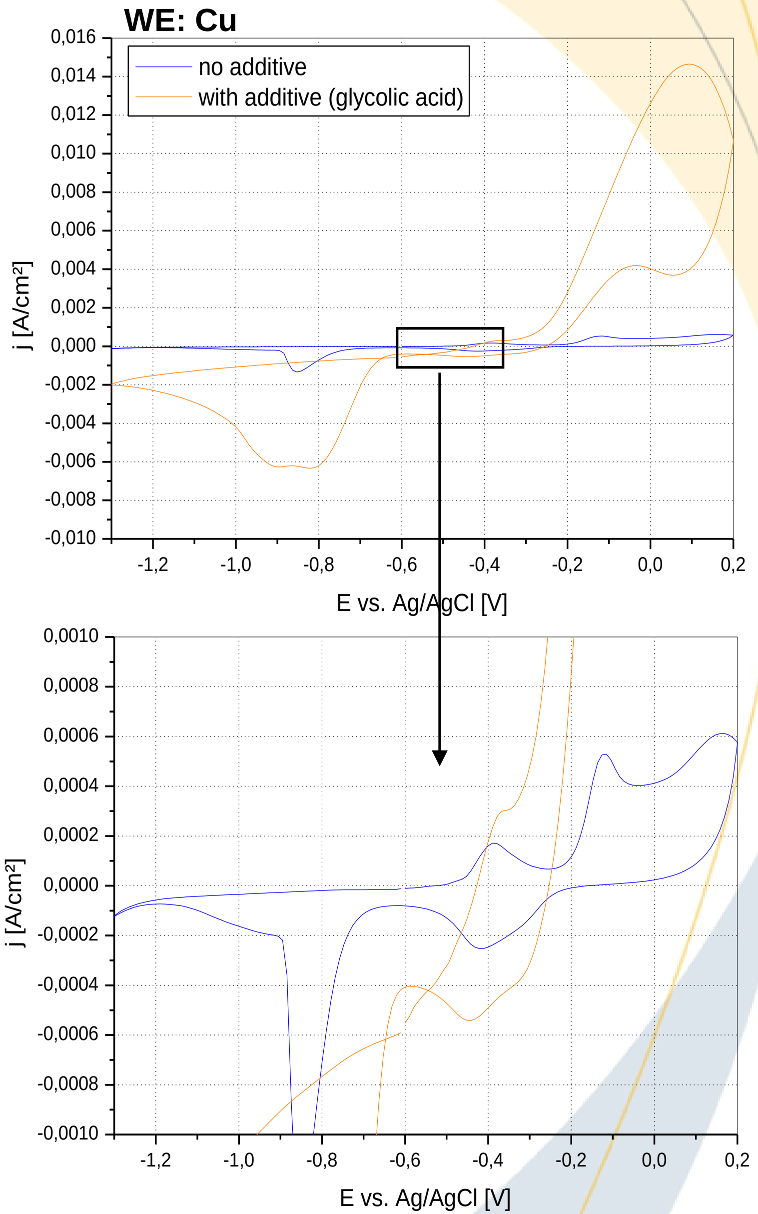


WE: Ni

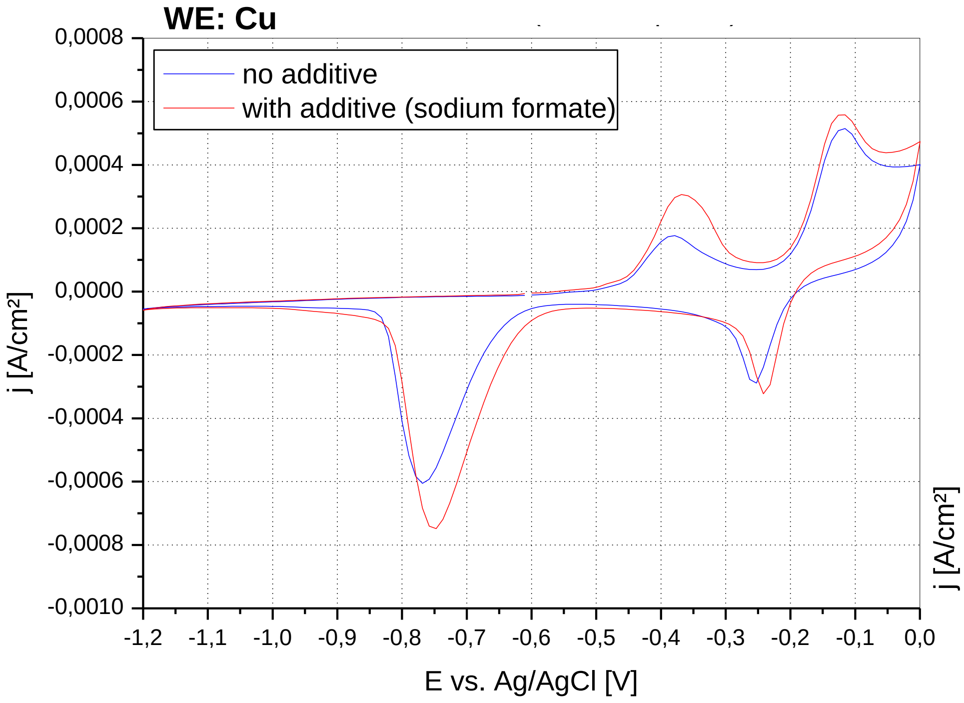
CV of $C_2H_4O_3$ (glycolic acid) at different working electrodes (WE)

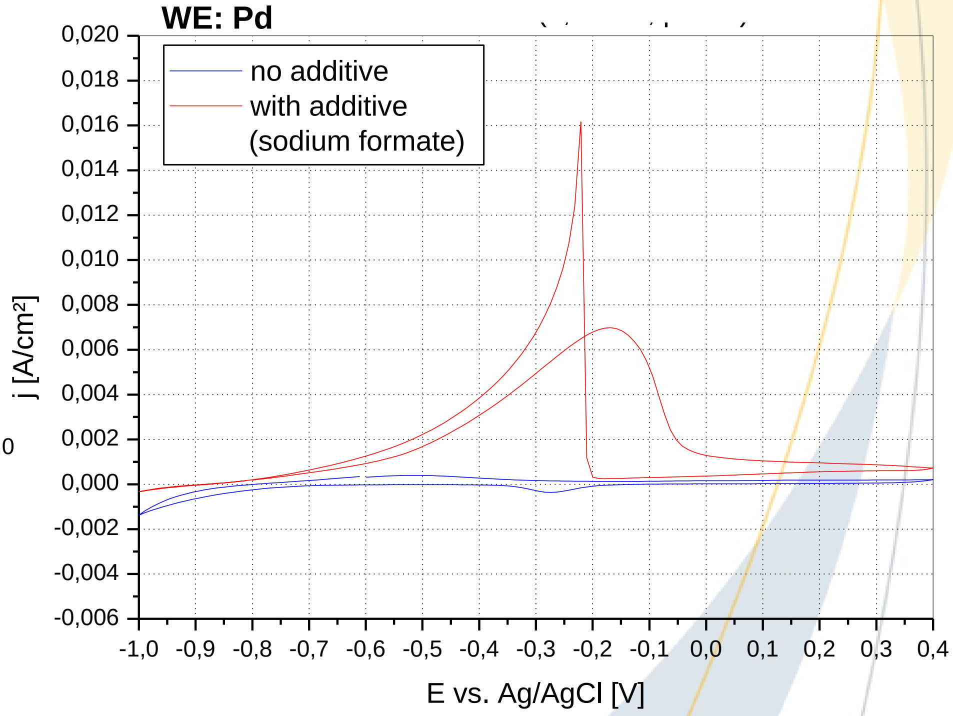
$c_{additive}$ = 0.3 mol/l; pH 13.0





CV of HCO_2Na (sodium formate) at different working electrodes (WE) $c_{additive}$ = 0.3 mol/l; pH 13.0





4 Conclusions

4 Conclusions

- Influence of the additive in the initial phase ↷ chemical „kick start“
- Oxidation reaction at the palladium surface
- Additional electrons
- High-quality copper coatings in spite of low reducing agent concentration
- Benefits:
  → Lower health risks
  → Lower costs (non-process-relevant side reactions)
  → Improved start-up behaviour

Thank you for your attention!