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RESEARCH ARTICLE

Effect of additive and current mode on surface morphology of palladium films from a non-aqueous deep eutectic solution (DES)

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Abstract Electrodeposition of palladium from a non-aqueous electrolyte solution [choline chloride/urea/palladium(II)chloride] has been carried out by direct and pulse current electroplating. In this study, the influence of an organic additive (nicotinic acid amide), current mode (direct current or pulse current deposition) and hydrodynamic on the surface morphology of electroplated palladium films was investigated. In order to determine the surface morphology and thickness of the electrodeposited palladium layers, a scanning electron microscope and an energy dispersive X-ray fluorescence spectroscope were used. In addition, the cell voltage during the different electrodeposition experiments was recorded and analysed. The experimental results showed that the surface morphology of the palladium deposits could be remarkably affected either by addition of the additive or by applying pulse current. Pulse plating and the selected inhibitor mutually interfere with each other, causing changes in the microstructure of the palladium deposits (e.g. smoothening or forming of micro-cracks). It was possible to optimise the palladium deposit quality by applying pulse current or by addition of the appropriate inhibitor.

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1 Introduction

Palladium coatings are widely used in industry, mainly in the electronics and jewellery industry [1, 2]. The most widely used solvent for plating is water because it is readily accessible, has a relatively high solubility for metal salts and high rates of mass transfer. However, there are some limitations associated with aqueous electrolytes. For instance, high pH values precipitates metal ions out as metal hydroxides, low pH promotes hydrogen evolution, causing problems such as hydrogen embrittlement.

Organic electrolyte solutions may not have the hydrogen evolution problem, but organic solvents often do not provide sufficient conductivity and solubility of metal salts. Alternatively, ionic liquids (IL) [3, 4] or deep eutectic solutions (DES) may provide the solution for the hydrogen problem. It has recently been shown that eutectic mixtures of choline chloride (ChCl) with urea or ethylene glycol form air and moisture stable liquids [5]. Various metal salts can be dissolved in this type of solvents [6–13]. In addition, mixtures of ChCl with urea are non-toxic, relatively low-priced and the single chemicals are widely available.

Therefore, the aim of a comprehensive study was to investigate the possible application of air-stable and non-aqueous IL or DES solutions for electrodeposition of palladium films, preferential free of cracks and hydrogen incorporation [14]. In the first part of this study basic physical data (density, moiety water content, viscosity, conductivity and electrochemical behaviour) of three different non-aqueous electrolyte systems (ChCl/ethylene glycol/$PdCl_2$, ChCl/urea/$PdCl_2$ and 1-butyl-3-methyl-imidazolium chloride-tetrafluoroborate/$PdCl_2$) have been investigated. Electrodeposition experiments revealed, that palladium films (layer thickness <0.2 µm) electroplated by direct current were fine grained, without micro-cracks and compact. The most promising results were obtained from the electrolyte system ChCl/urea/$PdCl_2$ [14]. However, increasing current density or plating time, to realise thicker Pd films (>0.5 µm), resulted in less compact and dense layers or dendritic structures of the Pd films. This phenomenon is although known for other metal electrolytes based on IL solutions.

Beside direct current deposition (DC) pulse current deposition (PP) is one of the techniques commonly used in electroplating. Pulse plating has several advantages over conventional plating [15, 16]. It is known that morphology, microstructure and properties of electrodeposits are impacted by the process parameters [17]. Therefore, pulse plating can improve deposit properties such as porosity, ductility, hardness and surface roughness. PP also yields a finer grained homogeneous surface appearance of the deposit, because a higher instantaneous current density is possible during deposition [18]. In addition, plating process parameters like current density, on time, off time and frequency can all be varied. Metal deposition from IL or DES-based electrolytes by PP has been performed for Al [19–21], Fe [12] and Ta [23]. The results for the Al deposition experiments indicate that the formation of dendritic structures was reduced, the surface morphology was smoother and thereby the optical appearance of the Al deposits was improved by the PP technique [19–21]. Smaller grains and thus more compact, dense and smooth deposits of Fe could be produced from DES solution (ChCl/urea/$FeCl_3$) by PP in comparison to DC deposition [12]. Recently, Ta was successfully electrodeposited from 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide by using potentiostatic square pulses, even at room temperature [22].

On the other hand, it is well known that the inclusion of even small amounts of certain additives in electrolyte solutions can influence the structure and properties of metal deposits. For commercial aqueous palladium electrolytes addition of surface active compounds (inhibitors) is conventional and widely spread. However, only little literature data are available about chemical formula and mechanism of surface active additives, typically used in commercial palladium electrolytes. The influence of selected inhibitors (sodium citrate, sodium benzoate, nicotinic acid and nicotinic acid amide) on the morphology of Pd electrodeposits from ammoniacal-based electrolytes was described in a former comprehensive study by Hedrich and Raub [23]. Their results showed that the influence of carboxylic acid derivatives on the surface morphology and structure of deposited Pd coatings increased from aliphatic (sodium citrate), aromatic (sodium benzoate) to hetero cyclic compounds (nicotinic acid). The addition of nicotinic acid or nicotinic acid amide to ammoniacal-based electrolytes improved notably the coating adhesion strength and produced glossy and smooth Pd coatings [23]. In contrast to aqueous electrolyte systems, the possible advantage and application potential of additives in ionic liquid or DES-based electrolytes is not investigated up to now.

In this paper, the authors have focused on electrodeposition of Pd from a DES without and with nicotinic acid amide as surface active compound by applying direct current (DC) or pulse current plating (PP).

2 Experimental

Choline chloride/urea solutions were prepared by mixing ChCl (Fluka, 97 %) with urea (Fluka, 99 %) in a molar ratio of 1:2. The mixtures (DES) were processed under partial vacuum at 80 °C for 2 h to remove traces of ammonia/amines and to reduce the moiety of water in the solutions. Palladium(II) was introduced to the basic solutions by dissolution of $PdCl_2$ ($PdCl_2$-anhydrous, Alfa Aesar, 99.9 % Pd) at 70 °C to result in yellow coloured $[PdCl_{4\text{-}x}]^{2-x}$ solution. To study the effect of additive on palladium deposition, 1.0 g L^{-1} of nicotinic acid amide ($C_6H_6N_2O$) was used. The ChCl/urea/$PdCl_2$ electrolyte has a relatively high viscosity of ~41.6 mPa s (at 70 °C) and an electrical conductivity of ~8.4 mS cm^{-1} (at 70 °C). The electrochemical window of the basic DES solution on glassy carbon was ~2.1 V (at 70 °C).

Bulk electrolysis experiments were performed in a two-electrode cell arrangement (Pd sheet anodes) with an electrolyte volume of 100 ml using a galvanostat from Voltalab (Model PST050). Generally, the electrolyte temperature was set to 70 ± 1 °C. Plating time was fixed to 90 min for all samples.

In the PP experiments a square-wave was used. Thus, a cathodic pulse of current density j_p was applied during the pulse time t_{on}, followed by a relaxation time t_{off} corresponding to the current interruption. The average current density j_{av}, is given by Eq. (1).

$$j_{av} = j_p t_{on}/(t_{on} + t_{off}) = j_p t_{on} \nu = j_p \theta \tag{1}$$

where ν is the pulse frequency and $\theta = t_{on}/(t_{on} + t_{off})$ is the duty cycle. The applied current density for DC plating was $j = 0.05$, 0.1 and 0.2 mA cm^{-2} and for PP plating $j_{av} = 0.1$ mA cm^{-2}.

Copper substrates (Cu rods: ∅ = 4 mm; Length = 40 mm) were degreased with acetone, polished with fine emery paper (SiC 800/2400), rinsed and dried. Before the electrolysis experiments the Cu substrates were activated by an oxidant solution (mixture of water/sodium peroxodisulfate/sulphur acid), washed with deionised water and dried with ethanol and nitrogen gas. Electrodeposition experiments were carried out with a rotating working electrode (surface area of the Cu substrate = 1.88 cm^2, electrode rotation between 0 and 800 rev min^{-1}) and under ambient air conditions. Secondary, the electrolyte solution in the electrolyte container was stirred by a magnetic stirrer at 200 rev min^{-1}.

The average thickness (L_{th}) and distribution of the electrodeposited Pd films was determined with energy dispersive X-ray fluorescence spectrometry—EDXRF (fischerscope XDAL, Fischer).

Surface analysis was carried out using a high resolution scanning electron microscope—HRSEM (LEO Supra 55VP, Zeiss).

3 Results and discussion

3.1 Direct current deposition (DC)

Bulk electrodeposition of Pd was performed on Cu substrates by DC at moderate hydrodynamic conditions (stirring of the electrolyte solution by a magnetic stirrer at 200 rev min^{-1} and rotating of the Cu electrode at a rotation speed of 50 rev min^{-1}). The applied current densities were 0.05, 0.1 and 0.2 mA cm^{-2}, respectively. The Pd(II) concentration of the electrolyte was 5 g L^{-1}.

The appearance of the electrodeposits varied with the applied current density. Grey till semibright metallic deposits were obtained at the employed current densities. Typical SEM micrographs of the surface morphology of the Pd films are shown in Fig. 1. As can be seen in Fig. 1a, b the palladium film at a current density of 0.05 mA cm^{-1} was nano-sized, nodular and compact. The deposit at a current density of 0.1 mA cm^{-2} was similar. Additionally, single-isolated Pd crystallite agglomerates were present on the surface (Fig. 1c, d). Deposition at a current density of 0.2 mA cm^{-2} increased the Pd particle size and revealed a coarse grained deposit (Fig. 1e, f). The average thickness of the Pd deposits was determined by EDXRF (average value of six single spot measurements). Though the current density increased from 0.05 to 0.2 mA cm^{-2} the measured average Pd film thickness was all about the same: $j =$ 0.05 mA cm^{-2} ($L_{th} = \sim 0.12$ μm), 0.1 mA cm^{-2} ($L_{th} = \sim 0.10$ μm) and 0.2 mA cm^{-1} ($L_{th} = \sim 0.11$ μm). This indicated that the metal reduction process was complicated under these DC plating conditions. The electrolyte system is predominantly controlled by mass transport of the reactive Pd species to the electrode surface. Additionally, at the initial stage of nucleation the Pd electrodeposition is affected by a promptly charge exchange reaction at the surface of the less noble Cu electrode (substrate) and the palladium complex ions in the electrolyte solution.

3.2 Direct current deposition (DC) with additive

In addition, bulk electrodeposition of Pd was performed on Cu substrates by DC using an electrolyte with nicotinic acid amide as additive under the same plating process conditions (hydrodynamic, temperature, current densities and Pd concentration).

The appearance of the electrodeposits varied with the applied current density. Grey till glossy metallic deposits were obtained at the employed current densities. The surface morphology of the electrodeposits varied remarkably from those presented in Fig. 1. Typical SEM micrographs of the surface morphology of these Pd films are shown in Fig. 2. As can be seen in Fig. 2a, b, the palladium deposit at a current density of 0.05 mA cm^{-2} was more nodular and coarse. The deposit at a current density of 0.1 mA cm^{-2} was nodular, compact and dense (Fig. 2c, d). Deposition at a current density of 0.2 mA cm^{-1} produced a nodular, compact and dense Pd surface with some nano-sized crystallites on the top of some nodules (Fig. 2e, f). In any case of applied current density, the apparent nodule size tends to increase by addition of the additive to the electrolyte due to the enhancement of crystallite growth rate. The average thickness of the Pd deposits increased with increasing current density. Obviously, the addition of a surface active compound to the electrolyte shifted the electrolyte system from a predominantly mass controlled to a predominantly kinetic controlled system.

3.3 Cell voltage during DC deposition experiments

Cyclic voltammetry data from the first part of our study showed that there was a remarkable nucleation overpotential necessary at the initial stage of electrodeposition of palladium from ChCl/urea/$PdCl_2$ solutions. A large peak potential separation $\left(\Delta E = E_p^c - E_p^a\right)$ indicated that the electrochemical reduction of Pd(II) in the cyclic voltammetry experiments is a mixed diffusion and kinetic controlled process [14].

Similar to current density-potential curves from voltammetry experiments (e.g. potential step voltammetry, linear sweep or cyclic voltammetry) the course of cell voltage during electrodeposition provides information about the plating process itself. From there, the cell voltage for all electrodeposition experiments was recorded to investigate the effect of process parameters and addition of additive on the deposition process. In the cell voltage measurement the applied current density was instantaneously jumped from j_1 (0 mA/cm^{-2}) to j_2 (0.05, 0.10 or

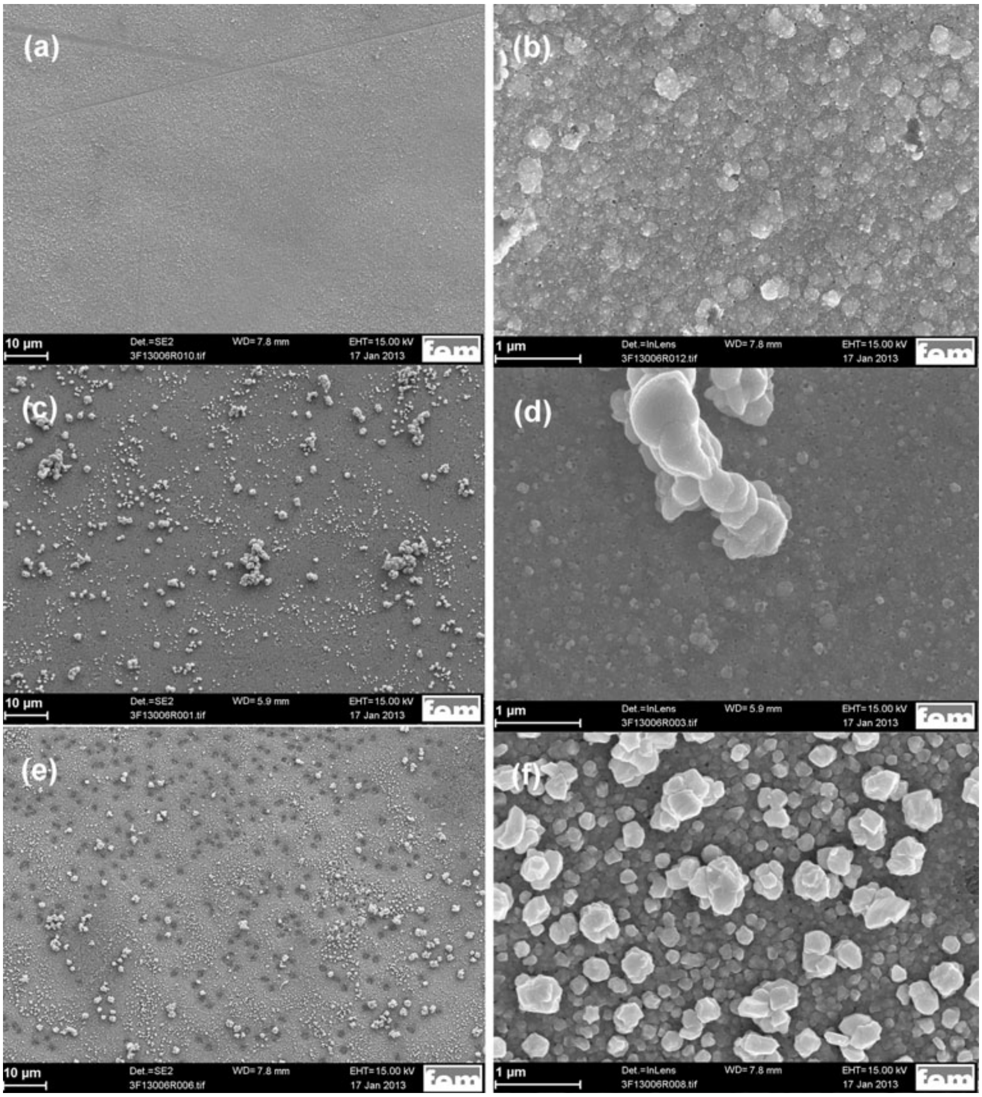

Fig. 1 Effect of current density on surface morphology of Pd films electrodeposited by DC without additive. **a**, **b** $j = 0.05$ mA cm^{-2}, L_{th} ~0.12 µm, **c**, **d** $j = 0.1$ mA cm^{-2}, L_{th} ~0.10 µm, **e**, **f** $j = 0.2$ mA cm^{-2}, L_{th} ~0.11 µm. Average thickness of deposits (EDXRF measurements) denoted as 'L_{th}' values. Rotation speed of the working electrode was 50 rev min^{-1}

0.20 mA/cm^{-2}) and kept constant during the plating time ($t = 90$ min). The resulting cell voltage (CV) was then recorded as a function of time.

Typical trends of CV during deposition of palladium by DC at various current densities are shown in Fig. 3a. Cell voltage became clearly more negative with increasing deposition current. In addition, the curves for the applied current densities at 0.1 and 0.2 mA cm^{-2} showed a remarkable decline of the CV within the first 10 min of plating followed by a gradual increase of the CV to pass into a plateau. The initial decline of the CV at higher current density may be partially attributed to the kind of complexation of Pd in the used electrolyte system. In a previous paper the authors indicated that there is evidence that Pd is less strong ligated as $[PdCl_{4-x}]^{2-x}$ complex anion in the ChCl/urea/PdCl$_2$ solution [14]. Whereas it is assumed, that Pd is stronger ligated as $[PdCl_4]^{2-}$ in solutions of 1-butyl-3-methylimidazolium chloride-tetrafluoroborate/PdCl$_2$ or ChCl/ethylene glycol/PdCl$_2$. So that, promptly charge exchange takes place by dipping of a less noble metal electrode into the ChCl/urea based electrolyte. Equally, a charge exchange reaction of weakly bonded palladium takes place in a strong acidic aqueous electrolyte (e.g. PdCl$_2$ dissolved in a solution containing hydrochloric acid) [25]. Therefore, it is assumed by the authors that under moderate hydrodynamic conditions the initial stage of nucleation is partially affected by a charge exchange reaction associated with a limited transport rate of Pd ions to the interface substrate/electrolyte with increasing applied current density.

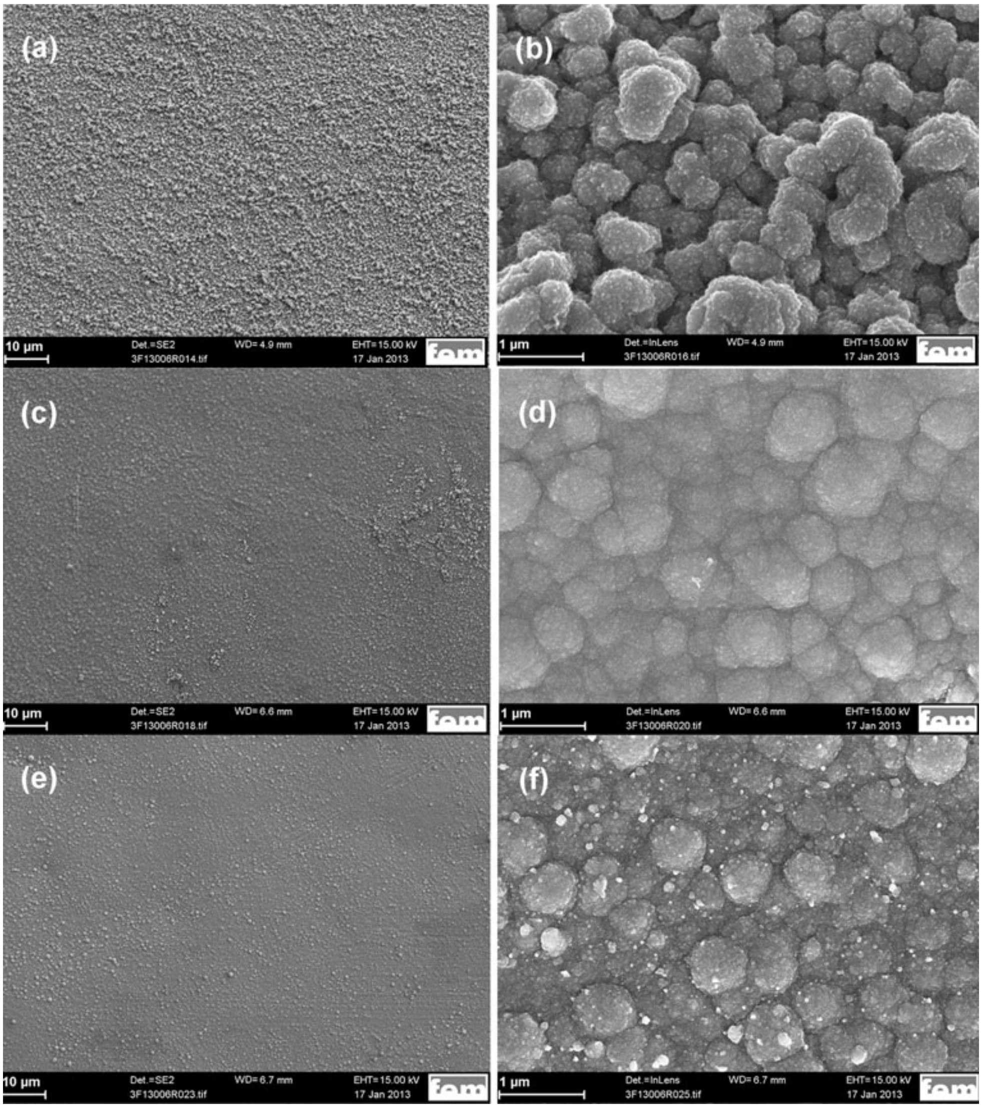

Fig. 2 Effect of current density and addition of additive (1.0 g L^{-1} nicotinic acid amide) on surface morphology of Pd films electrodeposited by DC. **a**, **b** $j = 0.05$ mA cm^{-2}, L_{th} ~0.12 µm, **c**, **d** $j =$ 0.1 mA cm^{-2}, L_{th} ~0.17 µm, **e**, **f** $j = 0.2$ mA cm^{-2}, L_{th} ~0.36 µm. Rotation speed of the working electrode was 50 rev min^{-1}

As can be seen in Fig. 3b, addition of nicotinic acid amide to the electrolyte solution had a clear impact on the course of CV. On the one hand the cell voltage became less negative for all three applied current densities and on the other hand the sharp decline of CV was considerably reduced within the first 10 min of plating at current densities of 0.1 and 0.2 mA cm^{-2}. Obviously, the process of electrocrystallisation was affected by the adsorption of nicotinic acid amide at the electrode surface. The shift to a more positive potential indicated that there is an adsorption of additive-metal ion complexes that directed the electrolyte system to be predominantly kinetic controlled.

Figure 4 represents values of cell voltage (CV) and average layer thickness (L_{th}) of the deposited Pd films from electrolytes with and without additive in dependence of the applied current density.

3.4 Pulse current deposition (PP)

Due to the relatively high viscosity and low conductivity of IL and DES, pulses with high frequencies (such as 10, 100 Hz or more) cannot be used successfully [19, 20, 22]. Beside electrolyte temperature hydrodynamic is one of the parameters typically used to improve the mass transfer of the reactive species from the bulk electrolyte solution to the electrode surface. A set of deposition experiments with varying rotation speed of the working electrode (0, 100, 200, 400 and 800 rev min^{-1}) revealed that the current

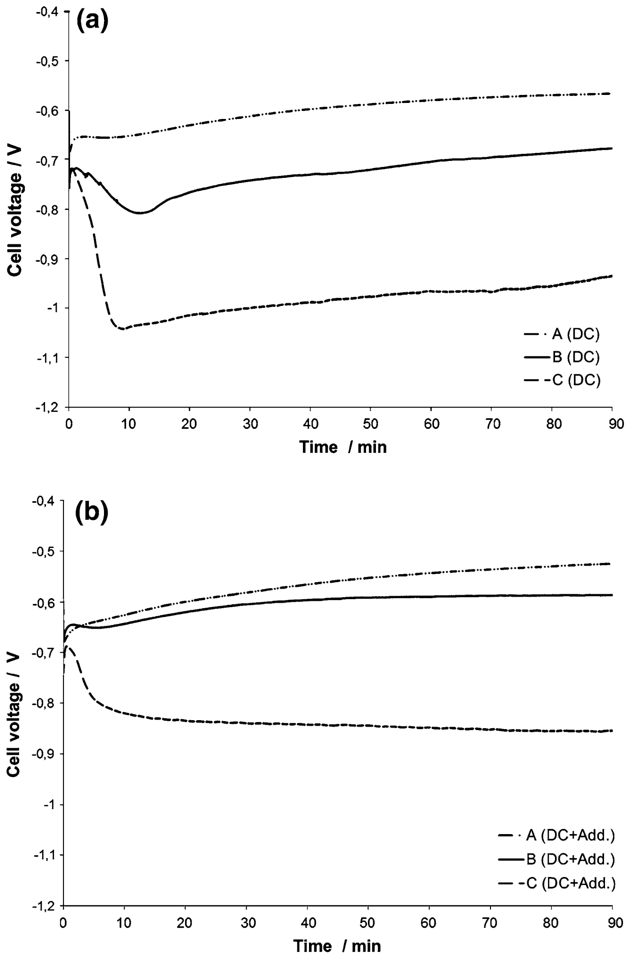

Fig. 3 Cell voltage–time responses during electrodeposition of Pd by DC. **a** Electrolyte without additive, **b** electrolyte with additive. *A* $j = 0.05$ mA cm^{-2}, *B* $j = 0.1$ mA cm^{-2}, *C* $j = 0.2$ mA cm^{-2}

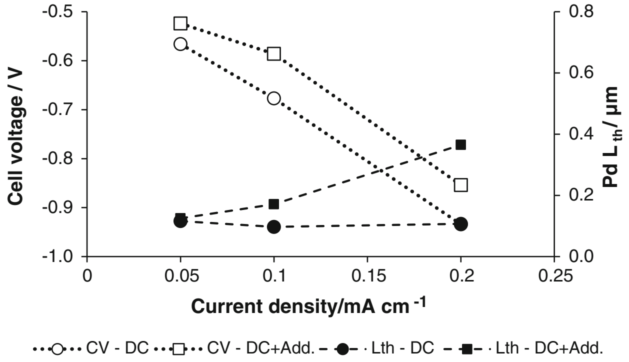

Fig. 4 Cell voltage and Pd film thickness after 90 min in dependence of the applied current density in electrolyte solutions with and without additive and an electrode rotation speed of 50 rev min^{-1}

efficiency (from 25 to ~100 %) and deposition rate of Pd could be remarkably increased at higher rotation speeds (data are not shown here). Therefore, supplementary pulse current deposition experiments were performed at raised hydrodynamic conditions (stirring of the electrolyte solution by a magnetic stirrer at 200 rev min^{-1} and rotating of the Cu electrode at a rotation speed of 800 rev min^{-1}) to enhance the rate of mass transport. Three different ratios of t_{on}/t_{off} with an average current density j_{av} of 0.1 mA cm^{-2} were applied. The applied current waveform was unipolar. The used pulse plating parameters are shown in Table 1.

Semibright metallic deposits were obtained. The SEM micrographs of the surface morphology of the Pd deposits are shown in Fig. 5. By comparison, the deposits showed fine grained, compact and smooth surfaces, particularly with some 'reliefs' present at the overall surface of the Pd deposits. The average thickness of the Pd films was influenced by the given pulse plating parameters: $t_{on}/t_{off} = 2{:}1$ ($L_{th} = \sim 0.33$ µm), $t_{on}/t_{off} = 1{:}1$ ($L_{th} = \sim 0.54$ µm) and $t_{on}/t_{off} = 1{:}2$ ($L_{th} = \sim 0.24$ µm).

3.5 Pulse current deposition (PP) with additive

Furthermore PP of Pd was performed from an electrolyte solution with nicotinic acid amide as surface active compound. The plating process parameters were equal to Table 1. Glossy metallic deposits were obtained. The SEM micrographs of the surface morphology of the Pd films are shown in Fig. 6. By comparison to Fig. 5, these deposits showed fine grained, compact and very smooth surfaces, occasionally with a network of micro-cracks. It is obvious that pulse plating and the additive mutually interfere with each other. The induced internal stress in the Pd films possibly arises from partial incorporation of additive and the uptake of small amounts of in situ generated hydrogen into the Pd films. It is known, that both fresh and used DES solutions, operated under ambient air, may contain residual water in the range of 0.5–3 wt% [14].

The average thickness of the Pd films was influenced by the given pulse plating parameters. In comparison to the results from PP without additive, the layer thickness of the Pd deposits has been increased by addition of the organic additive.

Worth mentioning is that nicotinic acid amide has a comparable effect on the micro-structure of electroplated Pd films from aqueous based electrolytes. For instance, in an early study Hedrich and Raub reported that addition of nicotinic acid amide to an ammoniacal $[Pd(NH_3)_4]Cl_2$-electrolyte produces smooth and glossy Pd films and the

Table 1 Pulse plating parameters for galvanostatic deposition of Pd

j_c (mA cm^{-2})	t_{on} (s)	t_{off} (s)	Frequency *f* (Hz)	Duty cycle θ (%)
0.15	2	1	0.33	66
0.20	1	1	0.50	50
0.30	1	2	0.33	33

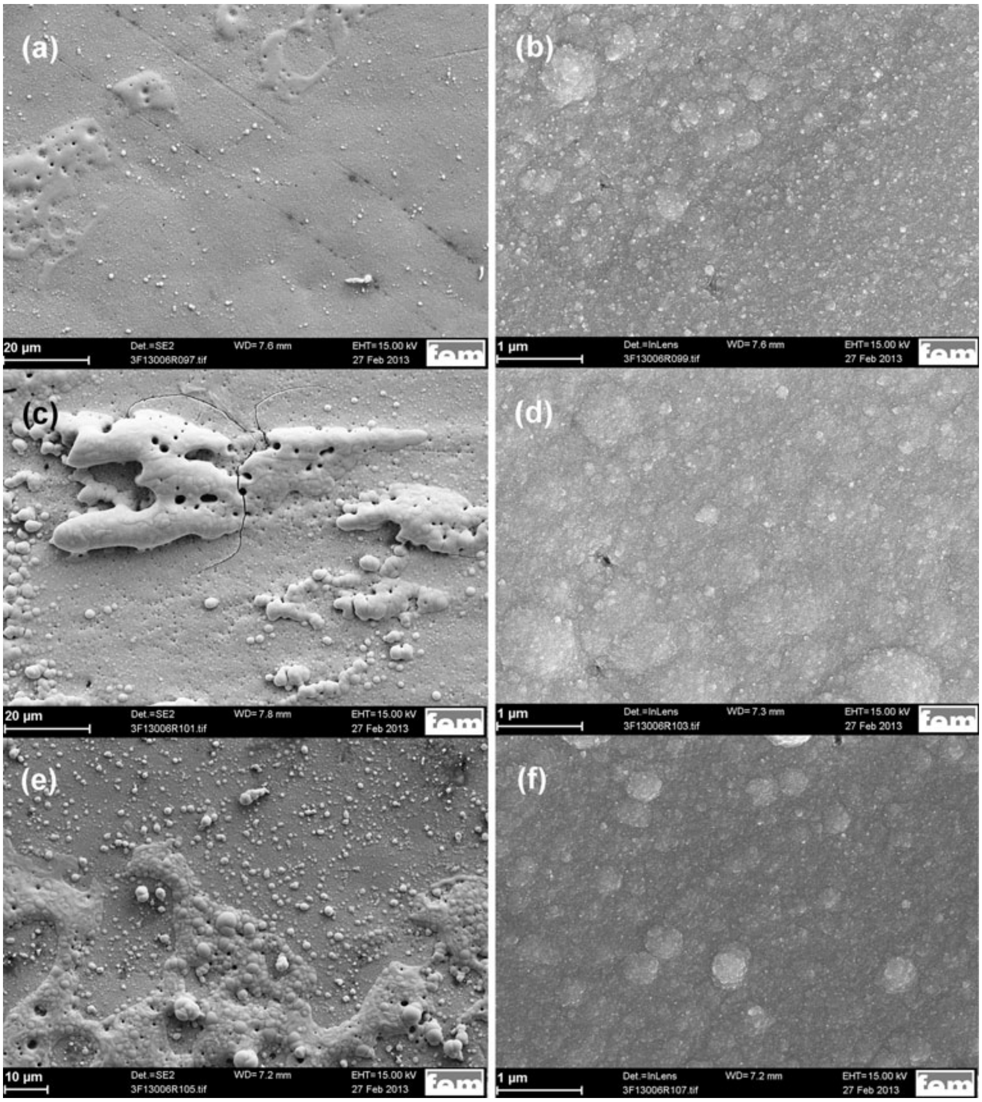

Fig. 5 Effect of pulse plating parameters on surface morphology of Pd films. **a**, **b** $t_{on}:t_{off} = 2$ s:1 s, L_{th} ~0.33 µm, **c**, **d** $t_{on}:t_{off} = 1$ s:1 s, L_{th} ~0.54 µm, **e**, **f** $t_{on}:t_{off} = 1$ s:2 s, L_{th} ~0.24 µm. Rotation speed of the working electrode was 800 rev min^{-1}

formation of a sharp <110> texture [23]. Therefore, it can be assumed that the effect of nicotine acid amid on the electrocrystallisation of palladium at the electrode surface is independent of the used solvent (aqueous ammoniacal $[Pd(NH_3)_4]Cl_2$-solution vs. quasi aprotic ChCl/urea/ $[PdCl_{4-x}]^{2-x}$ -solution).

3.6 Cell voltage during PP deposition

Trends of cell voltage during deposition of Pd by PP at various sets of t_{on}/t_{off} are shown in Fig. 7. At raised hydrodynamic conditions the cell voltage shifted to a more negative side by increasing the cathodic pulse current density j_c (from 0.15, 0.20 to 0.30 mA cm^{-2}). Addition of nicotinic acid amide to the electrolyte caused a further shift of CV to more negative values (Fig. 7b). This is in agreement with the fact, that the presence of a surface active compound (inhibitor) on an electrode surface affects the polarisation of the working electrode associated with a more negative deposition potential [24, 25]. Furthermore, the cell voltage achieved considerably faster steady-state behaviour (Fig. 7a, b).

Cell voltage and average layer thickness of Pd films deposited by PP from electrolytes with and without additive in dependence of the applied PP parameters are presented in Fig. 8.

To demonstrate the effect of the process parameter hydrodynamic on the course of CV and the surface quality of deposited Pd films data from PP experiments at moderate hydrodynamic condition (rotation speed of the electrode was 50 rev min^{-1}) are additionally presented. As can be seen from Fig. 7c, the CV shifted to much more

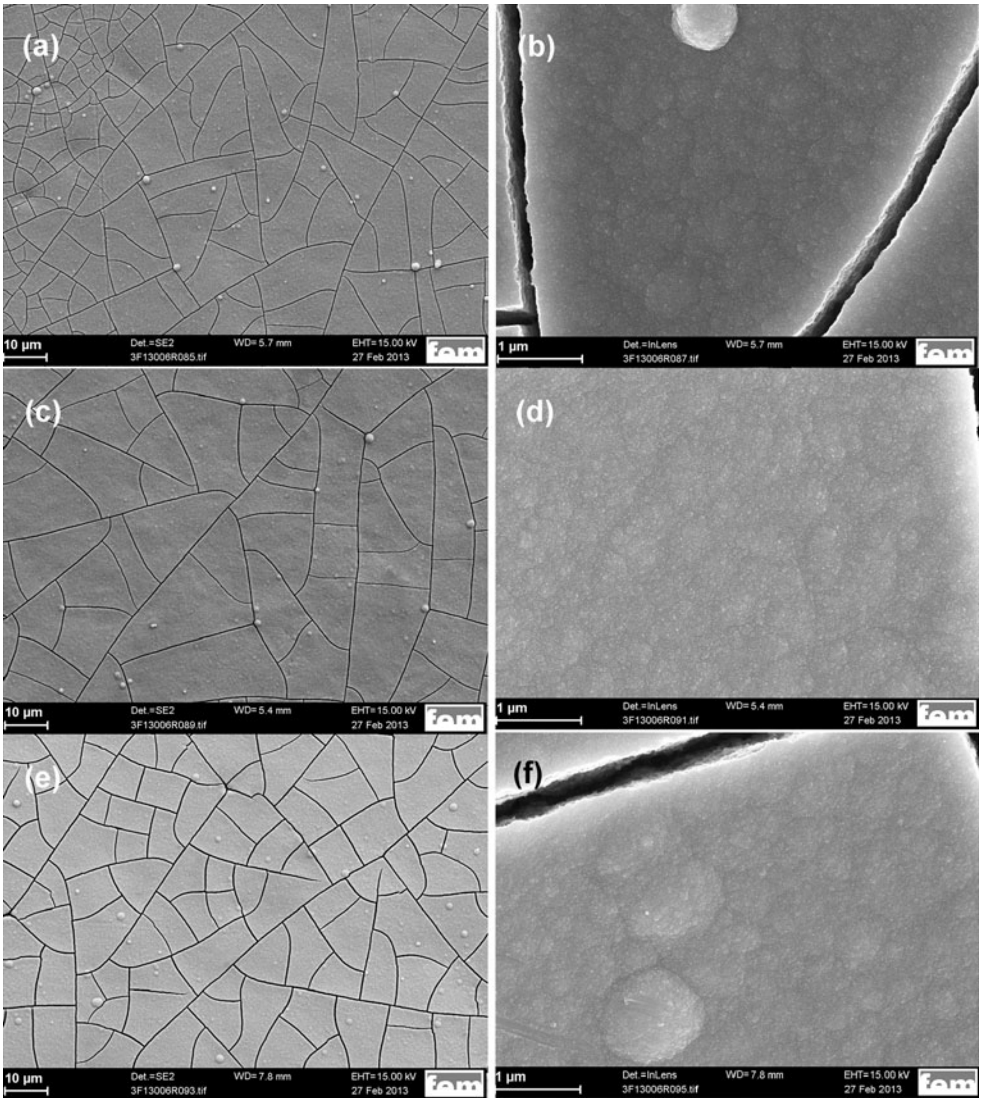

Fig. 6 Effect of pulse plating parameters and addition of additive (1.0 g L^{-1} nicotinic acid amide) on surface morphology of Pd films: **a**, **b** $t_{on}:t_{off} = 2$ s:1 s, $L_{th\text{-}av}$ ~0.54 µm, **c**, **d** $t_{on}:t_{off} = 1$ s:1 s, $L_{th\text{-}av}$ ~0.78 µm, **e**, **f** $t_{on}:t_{off} = 1$ s:2 s, $L_{th\text{-}av}$ ~0.33 µm. Rotation speed of the working electrode was 800 rev min^{-1}

negative values compared to the trends revealed at raised hydrodynamic conditions and the shape of the CV curves were similar to the CV curves obtained by DC deposition without additive (see Fig. 3a).

The photograph in Fig. 9 demonstrates the visible change in surface quality of Pd films electroplated by PP under moderate (Fig. 9a) and raised hydrodynamic conditions (Fig. 9b). The Pd film produced at higher electrode rotation speed is dense, smooth and glossy.

4 Conclusions

In this work, the effect of selected additive and different plating parameters (DC/PP) on the surface morphology and deposition rate of palladium through a non-aqueous electrolyte (ChCl/urea/$PdCl_2$) was studied. Depending on the electrolyte composition (with/without additive) and plating process parameters (DC/PP) palladium deposits with different surface morphologies were obtained.

At moderate hydrodynamic conditions DC deposition of Pd was predominantly controlled by mass transport of reactive Pd species to the electrode surface. Addition of nicotinic acid amide to the electrolyte solution affected the polarisation of the working electrode resulting in a higher current efficiency and metal deposition rate. The electrolyte system shifted to be predominantly kinetic controlled.

Additionally, PP deposition improved the metal deposition rate of Pd. Addition of nicotinic acid amide to the electrolyte system produced smooth and glossy Pd films.

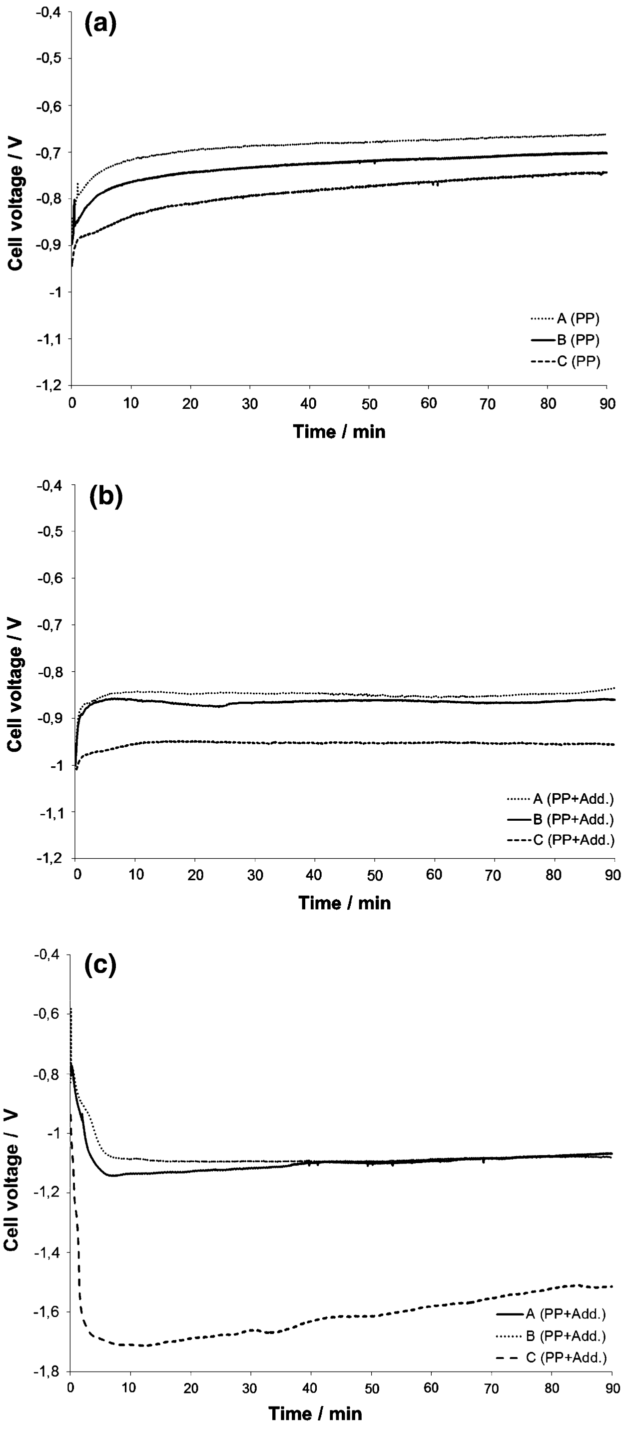

Fig. 7 Effect of PP process parameters and addition of additive (1.0 g L^{-1} nicotinic acid amide) on surface morphology of Pd films. **a** Electrolyte without additive and electrode rotation speed of 800 rev $\min^{-1}$, (**b**) electrolyte with additive and electrode rotation speed of 800 rev $\min^{-1}$, **c** electrolyte with additive and reduced electrode rotation speed of 50 rev $\min^{-1}$. *A* $t_{on}/t_{off} = 2{:}1$, *B* $t_{on}/t_{off} = 1{:}1$, *C* $t_{on}/t_{off} = 1{:}2$; $j_{av} = 0.1$ mA cm^{-2}

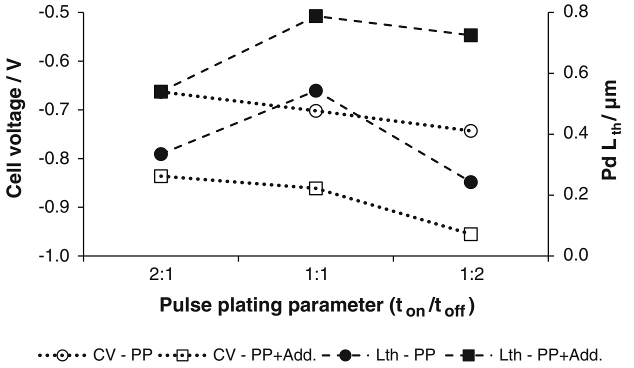

Fig. 8 Cell voltage and Pd film thickness after 90 min in dependence of the applied PP process parameters in electrolyte solution with and without additive and an electrode rotation speed of 800 rev $\min^{-1}$

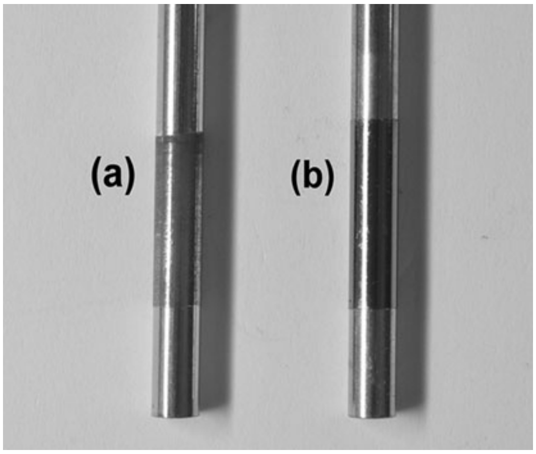

Fig. 9 Visible change in surface quality of Pd deposits. **a** Pd film deposited by PP ($t_{on}/t_{off} = 2$ s:1 s, $j_{av} = 0.1$ mA cm^{-2} and addition of 1.0 g L^{-1} nicotinic acid amide) with electrode rotation speed of 50 rev $\min^{-1}$ and **b** Pd film deposited by PP with electrode rotation speed of 800 rev $\min^{-1}$

Increased hydrodynamic process conditions raised the mass transport of reactive Pd species to the electrode surface and shifted the reduction potential to much more positive values. However, PP and the selected additive mutually interfere with each other, causing changes in the microstructure of the palladium deposits. Increasing the thickness of the electrodeposited Pd films (>0.5 µm) enhanced the formation of micro-cracks. Therefore, an optimisation of the parameters current density, electrolyte stirring and concentration of the additive is necessary to produce Pd films with adequate adhesion and high surface quality.

It could be demonstrated that raised hydrodynamic conditions and proper polarisation of the working electrode (addition of inhibitor) may key parameters to substantially improve the metal deposition rate and quality of palladium films electrodeposited from electrolytes based on non-aqueous deep eutectic solvents.

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