



# Electrodeposition of Pd–Se thin films

Monika Wojtysiak, Anna Jędraczka, Michał Stepień, Dawid Kutyla, Remigiusz Kowalik\*

AGH University of Science and Technology in Kraków, Faculty of Non-Ferrous Metals, Mickiewicza 30 Ave., Kraków 30-059, Poland

## ARTICLE INFO

### Keywords:

Electrodeposition  
Palladium  
Selenium palladium selenides  
Palladium chalcogenides  
Noble metal chalcogenides

## ABSTRACT

The presented research describes the electrochemical synthesis of Pd–Se thin films. The deposition process was accomplished in an aqueous chloride solution at a rotating disc electrode in the potential range from  $-0.4$  to  $-0.6$  V. The resulting coatings varied in both elemental and phase composition as well as surface morphology, depending on the potential. The difference is due to a change in the electrode reaction mechanism. A post-deposition heat treatment revealed the presence of Pd<sub>4</sub>Se in the coating deposited at  $-0.4$  V and Pd<sub>17</sub>Se<sub>15</sub> and Pd<sub>8</sub>Se in the other layers.

## 1. Introduction

The chalcogenides associated with noble metals have recently attracted increasing attention [1]. It turns out that, despite their chemical inertness, many compounds of noble metals with sulfur, selenium, or tellurium exist in nature [2]. The interest in these compounds arises primarily from their applicability as potential catalysts. However, current research attention is not due only to the excellent catalytic properties of the noble metals – the inspiration to investigate the possible synthesis of these materials was the spectacular catalytic properties of other chalcogenides, namely molybdenum and tungsten sulfides [3].

Considering the group of precious metal chalcogenides, compounds based on palladium and selenium are of particular interest. Palladium and selenium can form intermetallic compounds with different stoichiometric ratios: PdSe, PdSe<sub>2</sub>, Pd<sub>9</sub>Se<sub>2</sub>,  $\alpha$ Pd<sub>4</sub>Se,  $\beta$ Pd<sub>4</sub>Se, Pd<sub>7</sub>Se<sub>2</sub>, Pd<sub>7</sub>Se<sub>4</sub>, Pd<sub>17</sub>Se<sub>15</sub>, and Pd<sub>34</sub>Se<sub>11</sub> [2,4,5]. Thanks to their electrical properties, which include a wide tunable bandgap, unique pentagonal atomic structure, and excellent stability in air, these compounds have found application in the electronics industry as ultra-fast photonic devices, ultra-sensitive photodetectors, ultra-bound photodetectors and dye-sensitized solar cells [6–10]. Palladium and selenium compounds are very resistant to oxidation in acid solutions, although they are less stable in an alkaline environment. Therefore, the Pd<sub>4</sub>Se, Pd<sub>7</sub>Se<sub>4</sub>, and Pd<sub>17</sub>Se<sub>15</sub> phases show resistance to methanol during the ORR reaction. For this reason, Pd–Se compounds can be used as electrocatalysts in direct methanol fuel cells and the hydrogen evolution reaction [11–13].

Palladium–selenium compounds can be synthesized in a number of

ways, including chemical vapor deposition, selenization of palladium, molecular beam epitaxy, hydrothermal methods, thermolysis, solvothermal methods and exfoliation [6–9,11]. As far as we know, however, there have been no reports of the electrodeposition of Pd–Se thin films. Nevertheless, the electrochemical process has many advantages, e.g., control of the chemical and phase composition of coatings, as well as their thickness and morphology. Another characteristic of this method is its simplicity: the process can be carried out at a low temperature; it is easy to prepare the electrolyte; the process time is relatively short; and the costs of reagents and equipment are low. Moreover, electrodeposition of palladium and selenium has been widely described in the literature. Palladium deposition is possible from aqueous electrolytes over the entire pH range, including alkaline [14,15] and acidic [16,17] solutions. However, the electrochemical deposition mechanism is more complicated in the case of selenium due to its large number of oxidation states ( $-2$ ,  $+4$ ,  $+6$ ) [18–23]. Thus the process of selenium electrodeposition requires more attention, in particular due to its high reactivity and the possibility of interaction with the substrate [20]. Nevertheless, the precise control of the electrolysis parameters enables the electro-synthesis of numerous metal chalcogenides [23].

The present article describes for the first time a simple electrochemical method of depositing palladium–selenium coatings from chloride solutions. By controlling the deposition potential, it is possible to influence the elemental composition, phase structure, and morphology of the coatings, due to changes in the electrode reaction mechanism.

\* Corresponding author.

E-mail address: [rkowalik@agh.edu.pl](mailto:rkowalik@agh.edu.pl) (R. Kowalik).

<https://doi.org/10.1016/j.elecom.2021.107053>

Received 31 March 2021; Received in revised form 29 April 2021; Accepted 8 May 2021

Available online 13 May 2021

1388-2481/© 2021 The Author(s).

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 2. Experimental details

The Pd–Se coatings were synthesized from an electrolyte containing 0.008 M PdCl<sub>2</sub> (99% Aldrich), 0.008 M SeO<sub>2</sub> (99.999% Aldrich) and 0.2 M NaCl (CZDA POCH). The pH was adjusted to 2.0 by adding hydrochloric acid. Copper sheets covered with gold (2.84 cm<sup>2</sup>) were used as the substrate. The copper was chemically polished to remove impurities using a mixture of acids: HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and CH<sub>3</sub>COOH in a 1:1:1 vol ratio at a temperature of 70 °C for 40 s. The copper sheets were rinsed with deionized water and dried. Afterwards, a layer of gold at least 200 nm thick was sputtered onto the copper.

The deposition process was carried out in a three-electrode system, where Cu/Au was the working electrode, a Pt sheet was the counter electrode and the Ag/AgCl electrode served as the reference electrode. All the potentials in this article are given with respect to this electrode. The working electrode was embedded in a Teflon® holder and mounted as a rotating disc electrode on a Pine Research MSR Rotator. An AUTOLAB 302 N potentiostat controlled the electrolysis parameters. Electrodeposition was performed in the potential range from –0.4 to –0.6 V for 300 s at room temperature. A rotating disc with a rotational speed of 800 rpm was used. The deposited coatings were then annealed in a quartz tube at a temperature of 200 °C for 2 h under an argon atmosphere and then cooled to room temperature, also in the presence of the inert gas.

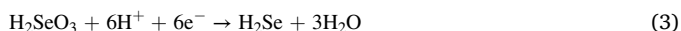
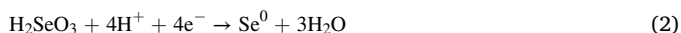
Before and after annealing, the surface morphology of the coatings was examined using a JEOL JCM-6000 NEOSCOPE scanning electron microscope. The elemental composition was determined by EDS analysis in at least three places: at the edges and in the center of the samples. Analyses were done at accelerating voltages of 10 kV from an area 0.4 mm<sup>2</sup> in size. The obtained results were averaged and their standard deviation was calculated. Phase analysis was carried out using the XRD method (Rigaku Miniflex II).

## 3. Results and discussion

The electrochemical deposition of both palladium and selenium from aqueous solutions has been described in the literature [14–25]. In the case of palladium, the deposition process in chloride solutions follows the reaction:



The process of selenium reduction from acidic solutions is more complex and, depending on the electrode potential, the following reactions may take place:



The reduction of selenous acid by the four-electron reaction (2) is possible at more positive potentials compared to the six-electron reaction (3) [26]. However, the potential at which the selenous acid reduction mechanism changes depends on many factors. First of all, naturally, it depends on the pH of the solution and the concentration of selenous acid [20]. Moreover, the selenous acid reduction mechanism also depends on any co-deposited metal and the electrode material [18,23,27]. Moreover, previously deposited selenium (Se<sup>0</sup>) may also be reduced to hydrogen selenide [20]. The selenous acid reduction reaction mechanism strongly influences the process of co-deposition of metals with selenium [28–31]. It also determines the composition, structure and surface morphology of the coatings. The palladium and selenium deposition process was carried out in the potential range between –0.4 and –0.6 V at pH 2. The potential range and pH were selected to observe the process of palladium and selenium co-deposition, where selenous acid can be reduced predominantly according to reaction (2) or (3). The

parameters were selected on the basis of our previous experience of the selenous acid reduction mechanism and co-deposition of selenium with metals from aqueous solutions at pH 2 [28–32]. Initial voltammetric tests indicate a possible switch in the selenous acid reduction mechanism from a four- to a six-electron reaction in the Pd–Se system at about –0.5 V (Fig. S1). However, a thorough interpretation of the results of voltammetric tests confirming the mechanism of palladium and selenium co-deposition goes far beyond the scope of this communication. A detailed electroanalytical analysis is currently being carried out in our laboratory.

### 3.1. EDS analysis

Table 1 shows the elemental composition of the coatings after deposition. All samples contain significantly more palladium than selenium. There is a characteristic tendency for a reduction in the palladium content with a simultaneous increase in the selenium concentration with more negative potential. There is a twofold increase in the selenium content of the samples deposited at –0.5 and –0.6 V compared with the coating obtained at –0.4 V.

### 3.2. XRD analysis

The XRD patterns for the as-deposited samples are shown in Fig. 1. In general, peaks related to the substrate (Cu/Au) are visible. Additionally, a single peak for palladium is observed at 39.75° for the sample deposited at –0.4 V. This element is present in the deposit as a separate phase. By contrast only peaks associated with the substrate are visible for samples deposited at –0.5 V and –0.6 V. It is difficult to determine whether the deposited palladium and selenium exist as separate phases or whether intermetallic compounds have been formed. The lack of peaks implies that the coatings have an amorphous structure.

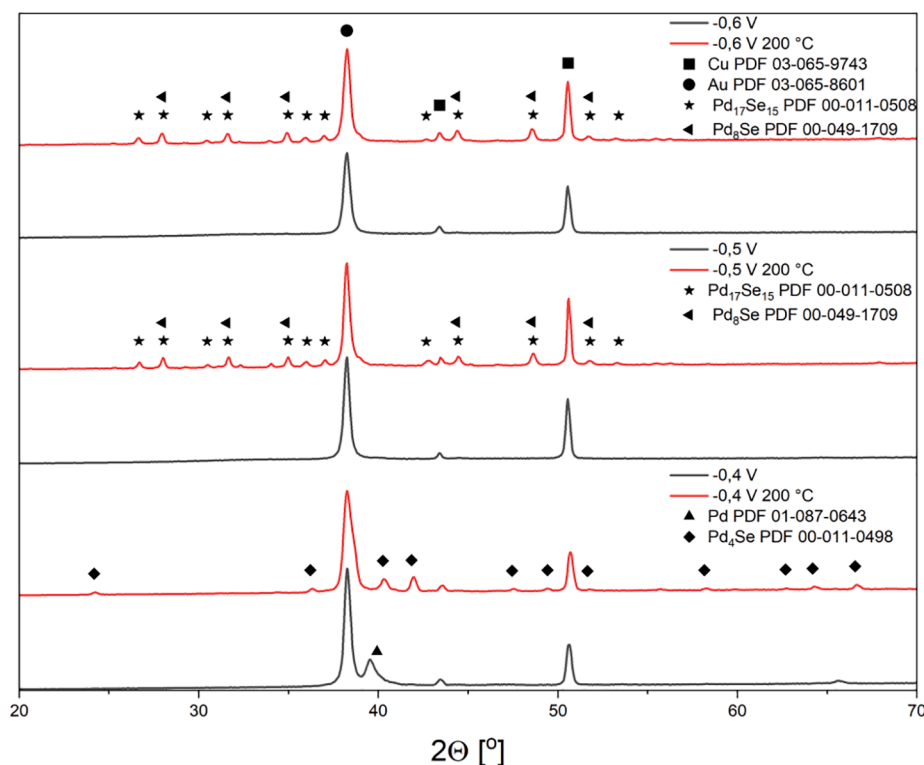
The samples were subjected to a heat treatment to improve the crystallinity of the deposits and subsequently reanalyzed using XRD. After the heat treatment at 200 °C, the composition of the coatings did not change significantly (Table 1), but a substantial difference was revealed between the samples deposited at –0.4 V and the samples obtained at –0.5 and –0.6 V. New peaks appeared compared to the as-deposited coatings. The common feature is still the dominance of the peaks attributed to the substrate. The palladium-related peak disappeared from the diffractogram obtained from the sample deposited at –0.4 V, and a series of peaks related to the Pd<sub>4</sub>Se phase appeared in its place. Overlapping peaks associated with the Pd<sub>17</sub>Se<sub>15</sub> and Pd<sub>8</sub>Se phases can be distinguished for coatings deposited at more negative potentials.

### 3.3. SEM analysis

The morphology of the coatings depends on the chemical composition and the phase structure (Fig. 2). There is a considerable difference between the layers deposited at –0.4 V and those deposited at more negative potentials. The former are grey with a metallic shine, while the latter are black and matt. Electron microscopy studies reveal the reason for such a significant difference in the appearance of the coatings. The

**Table 1**  
Elemental composition of coatings electrodeposited at different potentials from bath: 0.008 M PdCl<sub>2</sub>, 0.008 M H<sub>2</sub>SeO<sub>3</sub>, 0.2 M NaCl, pH = 2 on Cu/Au electrode: (a), (c), (e) before annealing; (b), (d), (f) after annealing at 200 °C for 2 h in an argon atmosphere.

|     | E vs Ag/AgCl (V) | Pd <sub>av</sub> (% at.) |      | Se <sub>av</sub> (% at.) |      |
|-----|------------------|--------------------------|------|--------------------------|------|
| (a) | –0.4             | 83.4                     | ±0.6 | 16.6                     | ±0.6 |
| (b) |                  | 78.4                     | ±2.4 | 21.6                     | ±2.4 |
| (c) | –0.5             | 67.6                     | ±1.5 | 32.5                     | ±1.5 |
| (d) |                  | 66.6                     | ±3.7 | 33.4                     | ±3.7 |
| (e) | –0.6             | 65.0                     | ±0.9 | 35.0                     | ±0.9 |
| (f) |                  | 63.9                     | ±3.0 | 36.1                     | ±3.0 |



**Fig. 1.** XRD patterns of coatings electrodeposited at different potentials from a bath containing 0.008 M  $\text{PdCl}_2$ , 0.008 M  $\text{H}_2\text{SeO}_3$ , 0.2 M NaCl, pH = 2 on a Cu/Au electrode: before annealing (black lines) and after annealing at 200 °C for 2 h in an argon atmosphere (red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sample deposited at  $-0.4$  V is compact and composed of small globules very tightly attached, which is typical of many metallic coatings. In contrast, the deposits obtained at more negative potentials are porous and composed of bunches of needles, which explains the lack of shine.

The characteristics of the coatings described above are related to the reaction mechanism. The co-deposition of palladium and selenium proceeds according to reactions (1) and (2). The slow kinetics of selenous acid reduction by the four-electron process is responsible for the high palladium content of the deposit [25]. Phase analysis confirms only the presence of metallic palladium. The lack of selenium peaks is related to the amorphous structure, which is characteristic of selenium coatings obtained by electrochemical methods [20,28–33]. Only heat treatment forces the reaction between palladium and selenium, and consequently the synthesis of  $\text{Pd}_4\text{Se}$ . The elemental composition is very close to the stoichiometry of this compound. The disappearance of the peak associated with pure palladium confirms that the synthesis reaction has taken place. It should also be noted that the heat treatment did not significantly affect the content of palladium and selenium.

The increase in selenium content of coatings deposited at  $-0.5$  and  $-0.6$  V is related to a change in the selenous acid reduction mechanism. When the potential is more negative than  $-0.4$  V, the reduction of selenous acid proceeds according to the 6-electron mechanism (3). The final product of reaction (3) is hydrogen selenide. When palladium is deposited simultaneously, the formation of hydrogen selenide is hindered due to rapid coverage by Pd before the Se atoms could be reduced to  $\text{H}_2\text{Se}$ . It is difficult to resolve whether the proposed mechanism implies the direct synthesis of intermetallic compounds or whether palladium and selenium exist in the coating as separate phases at the present stage of research. Confirmation of the above theory undoubtedly requires further investigation, which will confirm the mechanism of electrode reactions during the co-deposition of selenium and palladium.

Structural examination of the coatings after deposition did not reveal any crystalline phase. Unlike the layer deposited at  $-0.4$  V, no peak was recorded that would indicate the presence of crystalline palladium. The

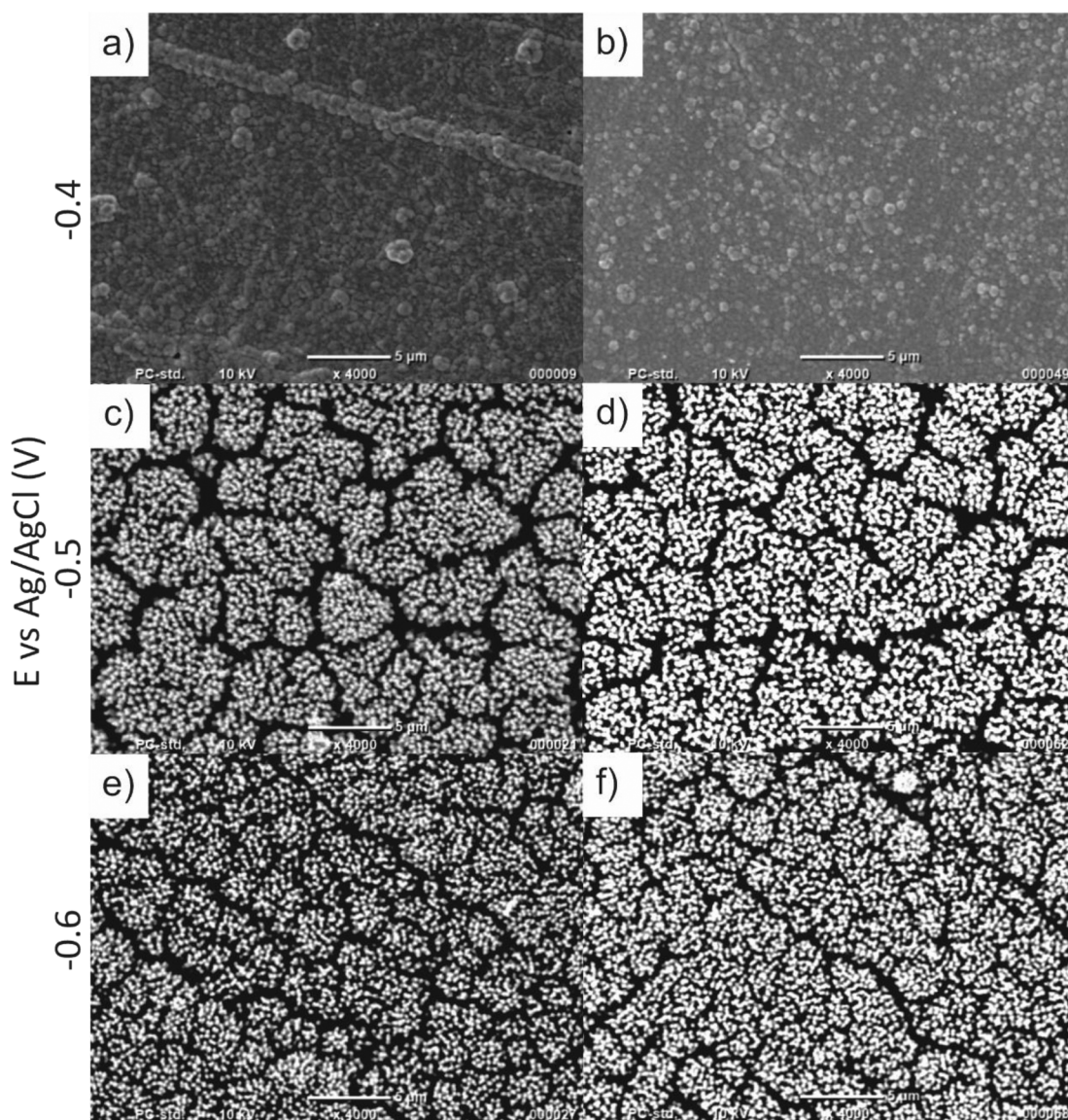
lack of this peak is related to a decrease in the palladium content of the deposit. The heat treatment revealed a mixture of palladium–selenium compounds, namely  $\text{Pd}_{17}\text{Se}_{15}$  and  $\text{Pd}_8\text{Se}$ . The phase analysis of the tested coatings is complicated due to the overlapping of peaks from both intermetallic compounds. All peaks fit perfectly into the  $\text{Pd}_{17}\text{Se}_{15}$  phase (except peaks related to the substrate). However, the elemental analysis shows an excess of palladium. The other  $\text{Pd}_8\text{Se}$  phase would explain the excess palladium in the coatings.

The conducted research indicates a substantial difference between the coatings deposited at  $-0.4$  V and those deposited at more negative potentials. The increase in selenium content, the lack of crystalline palladium and the change in the morphology of the coatings suggest a change of mechanism related to selenous acid reduction. Clarification of the mechanism of the electrode reactions undoubtedly requires further research.

#### 4. Conclusions

This report presents a straightforward method of synthesizing palladium selenides by electrodeposition. The results show that it is possible to control the co-deposition of palladium and selenium from aqueous solutions. The composition and the morphology of the coatings strongly depend on the applied potential. Studies of the separate reactions show that the co-deposition of selenium and palladium takes place at a potential of  $-0.4$  V and does not lead directly to the synthesis of palladium chalcogenides. However, heat treatment at 200 °C is sufficient to obtain an intermetallic compound corresponding to the stoichiometry of the deposited coating i.e.,  $\text{Pd}_4\text{Se}$ . Furthermore, changing the potential in a more negative direction changes the mechanism of palladium and selenium co-deposition. These layers have a higher content of selenium than those deposited at  $-0.4$  V. The as-deposited coatings have an amorphous structure, while the heat treatment produces a mixture of  $\text{Pd}_{17}\text{Se}_{15}$  and  $\text{Pd}_8\text{Se}$  phases.





**Fig. 2.** SEM micrographs of coatings electrodeposited at different potentials from a bath containing 0.008 M  $\text{PdCl}_2$ , 0.008 M  $\text{H}_2\text{SeO}_3$ , 0.2 M NaCl, pH = 2, on a Cu/Au electrode: (a), (c), (e) before annealing, (b), (d), (f) after annealing at 200 °C for 2 h in an argon atmosphere.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

This work was supported by the Polish National Science Centre under grant 2016/21/B/ST8/00431.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.elecom.2021.107053>.

### References

- [1] R. Kempt, A. Kuc, T. Heine, Two-dimensional noble-metal chalcogenides and phosphochalcogenides, *Angew. Chem. Int. Ed.* 59 (24) (2020) 9242–9254, <https://doi.org/10.1002/anie.201914886>.
- [2] S. Bordier, A. Chocard, S. Gossé, Thermodynamic assessment of the palladium–selenium (Pd–Se) system, *J. Nucl. Mater.* 451 (1–3) (2014) 120–129, <https://doi.org/10.1016/j.jnucmat.2014.03.044>.
- [3] T.F. Jaramillo, K.P. Jorgensen, J. Bonde, J.H. Nielsen, S. Hørch, I. Chorkendorff, Identification of active edge sites for electrochemical  $\text{H}_2$  evolution from  $\text{MoS}_2$  nanocatalysts, *Science* 317 (5834) (2007) 100–102, <https://doi.org/10.1126/science.1141483>.
- [4] H. Okamoto, The Pd–Se (palladium–selenium) system, *J. Phase Equil.* 13 (1) (1992) 69–72, <https://doi.org/10.1007/BF02645382>.
- [5] D. Sandip, J.V. Kumar, Platinum group metal chalcogenides, *Platin. Met. Rev.* 48 (2004) 16–29.
- [6] L.-H. Zeng, D. Wu, S.-H. Lin, C. Xie, H.-Y. Yuan, W. Lu, S.P. Lau, Y. Chai, L.-B. Luo, Z.-J. Li, Z.-J. Li, Y.H. Tsang, Controlled synthesis of 2D palladium diselenide for sensitive photodetector applications, *Adv. Funct. Mater.* 29 (2019) 1806878, <https://doi.org/10.1002/adfm.201806878>.
- [7] H. Zhang, P. Ma, M. Zhu, W. Zhang, G. Wang, S. Fu, Palladium selenide as a broadband saturable absorber for ultra-fast photonics, *Nanophotonics* 9 (2020) 2557–2567, <https://doi.org/10.1515/nanoph-2020-0116>.
- [8] A.D. Oyedele, S. Yang, L. Liang, A.A. Puretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A.W. Ghosh, Z. Liu, C.M. Rouleau, B.G. Sumpter, M.F. Chisholm, W. u. Zhou, P.D. Rack, D.B. Geohegan, K. Xiao,  $\text{PdSe}_2$ : pentagonal two-dimensional layers with high air stability for electronics, *J. Am. Chem. Soc.* 139 (40) (2017) 14090–14097, <https://doi.org/10.1021/jacs.7b04865>. PMID - 28873294.
- [9] Q. Liang, Q. Wang, Q. Zhang, J. Wei, S.X. Lim, R. Zhu, J. Hu, W. Wei, C. Lee, C. Sow, W. Zhang, A.T.S. Wee, High-performance, room temperature, ultra-broadband photodetectors based on air-stable  $\text{PdSe}_2$ , *Adv. Mater.* 31 (2019) 1807609, <https://doi.org/10.1002/adma.201807609>. PMID - 31025440.

- [10] Y. Duan, Q. Tang, B. He, L. Yu, Transparent counter electrode from palladium selenide for bifacial dye-sensitized solar cell, *Mater. Lett.* 160 (2015) 511–514, <https://doi.org/10.1016/j.matlet.2015.08.035>.
- [11] S. Kukunuri, P.M. Austeria, S. Sampath, Electrically conducting palladium selenide ( $\text{Pd}_4\text{Se}$ ,  $\text{Pd}_{17}\text{Se}_{15}$ ,  $\text{Pd}_7\text{Se}_4$ ) phases: synthesis and activity towards hydrogen evolution reaction, *Chem. Commun.* 52 (1) (2016) 206–209, <https://doi.org/10.1039/C5CC06730H>.
- [12] S. Kukunuri, K. Naik, S. Sampath, Effects of composition and nanostructuring of palladium selenide phases,  $\text{Pd}_4\text{Se}$ ,  $\text{Pd}_7\text{Se}_4$  and  $\text{Pd}_{17}\text{Se}_{15}$ , on ORR activity and their use in Mg–air batteries, *J. Mater. Chem. A* 5 (9) (2017) 4660–4670, <https://doi.org/10.1039/C7TA00253J>.
- [13] J.M. Mora-Hernández, K. Vega-Granados, L.A. Estudillo-Wong, C. Canaff, N. Alonso-Vante, Chemistry, surface electrochemistry, and electrocatalysis of carbon-supported palladium-selenized nanoparticles, *ACS Appl. Energy Mater.* 3 (11) (2020) 11434–11444, <https://doi.org/10.1021/acsaem.0c02370>.
- [14] R. Le Penven, W. Levason, D. Pletcher, Studies of the electrodeposition of palladium from baths based on  $[\text{Pd}(\text{NH}_3)_2\text{X}_2]$  salts. I.  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  baths, *J. Appl. Electrochem.* 20 (3) (1990) 399–404, <https://doi.org/10.1007/BF01076048>.
- [15] K. Mech, P. Zabiński, R. Kowalik, K. Fitzner, Voltammetric study of electro-reduction of tetraamminepalladium(II) onto gold electrode, *J. Electroanal. Chem.* 685 (2012) 15–20, <https://doi.org/10.1016/j.jelechem.2012.08.035>.
- [16] M.E. Quayum, S. Ye, K. Uosaki, Mechanism for nucleation and growth of electrochemical palladium deposition on an Au(111) electrode, *J. Electroanal. Chem.* 520 (1–2) (2002) 126–132, [https://doi.org/10.1016/S0022-0728\(02\)00643-5](https://doi.org/10.1016/S0022-0728(02)00643-5).
- [17] K. Mech, P. Zabiński, R. Kowalik, K. Fitzner, Kinetics and mechanism of  $[\text{PdCl}_x(\text{H}_2\text{O})_{4-x}]^{2-x}$  ( $x = 3, 4$ ) complexes electro-reduction, *J. Electrochem. Soc.* 160 (10) (2013) H770–H774, <https://doi.org/10.1149/2.007311jes>.
- [18] R. Kowalik, Microgravimetric studies of selenium electrodeposition onto different substrates, *Arch. Metall. Mater.* 59 (2014) 871–877, <https://doi.org/10.2478/amm-2014-0147>.
- [19] R. Kowalik, The voltammetric analysis of selenium electrodeposition from  $\text{H}_2\text{SeO}_3$  solution on gold electrode, *Arch. Metall. Mater.* 60 (2015) 57–63, <https://doi.org/10.1515/amm-2015-0009>.
- [20] K. Kolczyk, R. Kowalik, K. Mech, P. Zabiński, Electrochemical deposition of selenium on copper, *Key Eng. Mater.* 682 (2016) 189–196, <https://doi.org/10.4028/www.scientific.net/KEM.682.189>.
- [21] B. Rasche, H.M.A. Amin, S.J. Clarke, R.G. Compton, Polyselenides on the route to electrodeposited selenium, *J. Electroanal. Chem.* 835 (2019) 239–247, <https://doi.org/10.1016/j.jelechem.2019.01.015>.
- [22] R.W. Andrews, D.C. Johnson, Voltammetric deposition and stripping of selenium (IV) at a rotating gold-disk electrode in 0.1M perchloric acid, *Anal. Chem.* 47 (2) (1975) 294–299, <https://doi.org/10.1021/ac60352a005>.
- [23] M. Bouroushian, *Electrochemistry of Metal Chalcogenides*, Springer, Berlin Heidelberg, Berlin, Heidelberg (2010), <https://doi.org/10.1007/978-3-642-03967-6>.
- [24] A. von Hippel, M.C. Bloom, The electroplating of metallic selenium, *J. Chem. Phys.* 18 (9) (1950) 1243–1251, <https://doi.org/10.1063/1.1747918>.
- [25] T.E. Lister, J.L. Stickney, Atomic level studies of selenium electrodeposition on gold(111) and gold(110), *J. Phys. Chem.* 100 (50) (1996) 19568–19576, <https://doi.org/10.1021/jp9621540>.
- [26] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, National Association of Corrosion Engineers, Houston, Tex, 1974.
- [27] J.L. Stickney, Electrochemical atomic layer epitaxy (EC-ALE): Nanoscale control in the electrodeposition of compound semiconductors, in: *Advances in Electrochemical Science and Engineering*, John Wiley & Sons, Ltd, 2001, pp. 1–105, <https://doi.org/https://doi.org/10.1002/3527600264.ch1>.
- [28] R. Kowalik, K. Fitzner, Analysis of the mechanism for electrodeposition of the ZnSe phase on Cu substrate, *J. Electroanal. Chem.* 633 (1) (2009) 78–84, <https://doi.org/10.1016/j.jelechem.2009.04.029>.
- [29] R. Kowalik, P. Zabiński, K. Fitzner, Electrodeposition of ZnSe, *Electrochim. Acta* 53 (21) (2008) 6184–6190, <https://doi.org/10.1016/j.electacta.2007.12.009>.
- [30] R. Kowalik, H. Kazimierzczak, P. Zabiński, Electrodeposition of cadmium selenide, *Mater. Sci. Semicond. Process.* 50 (2016) 43–48, <https://doi.org/10.1016/j.mssp.2016.04.009>.
- [31] D. Kutyla, K. Kolczyk, P. Zabiński, R. Kowalik, Electrodeposition of  $\text{Ni}_3\text{Se}_2$ , *J. Electrochem. Soc.* 164 (12) (2017) D700–D706, <https://doi.org/10.1149/2.1251712jes>.
- [32] A.M. Kwiecińska, D. Kutyla, K. Kolczyk-Siedlecka, K. Skibińska, P. Zabiński, R. Kowalik, Electrochemical analysis of co-deposition cobalt and selenium, *J. Electroanal. Chem.* 848 (2019) 113278, <https://doi.org/10.1016/j.jelechem.2019.113278>.
- [33] R. Kowalik, K. Szaciłowski, P. Zabiński, Photoelectrochemical study of ZnSe electrodeposition on Cu electrode, *J. Electroanal. Chem.* 674 (2012) 108–112, <https://doi.org/10.1016/j.jelechem.2012.03.002>.