

## STRUCTURE AND ELECTROCATALYTIC PROPERTIES OF AMORPHOUS COBALT–SULPHIDE FILMS ON FTO SUBSTRATE

R. MARDOSAITE, E. VALATKA \*

*Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilenu str. 19, LT-50254 Kaunas, Lithuania*

Amorphous cobalt–sulphide (Co–S) films on fluorine-doped tin oxide (FTO) substrate were prepared by potentiodynamic deposition using thiourea and cobalt chloride electrolyte. The influence of synthesis conditions (number of deposition cycles, electrolysis bath temperature) on structure, morphology and composition of as-deposited Co–S films was studied. The possible mechanism of electrodeposition is discussed. Structural and morphological characterization of the prepared films was carried out by means of scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), UV-Vis diffuse reflectance (UV-Vis DR) and infrared spectroscopy (FT–IR) techniques. The electrocatalytic performance of Co–S films in hydrogen evolution reaction (HER) was evaluated in phosphate buffer solutions.

(Received February 28, 2017; Accepted May 3, 2017)

*Keywords:* Cobalt sulphide, Thiourea, Electrochemical deposition, Electrocatalytic water splitting

### 1. Introduction

Nanostructured metal chalcogenides are regarded as the most prominent candidates for various energy-related applications, such as fuel or solar cells, supercapacitors, lithium-ion batteries, (photo)electrochemical water splitting [1-3]. A variety of synthesis methods is used in order to design innovative nanomaterials with controlled morphology, size, composition and structure. For example, Gao et al. [3] systematically summarized the recent progress made concerning fifteen typical methods of liquid-phase synthesis and modification of nanostructured metal chalcogenides. Currently, tremendous efforts have been made in order to improve the efficiency of (photo)electrochemical water splitting using earth-abundant inorganic electrocatalysts [4-6].

The desired electrocatalytic material should cover long-term stability combined with resistance to corrosion in aqueous media, stimulation of hydrogen evolution reaction (HER) with low over potential and a high efficiency achievement in a broad range of solar spectrum [7, 8]. Numerous experiments have established that inorganic catalysts can succeed in the majority of the necessary features. However, they have been found to suffer from multifunctional imperfections and/or are limited to work only in strongly acidic or basic media [8].

It is generally accepted that utilization of earth-abundant inorganic materials can help to replace platinum as the most effective but unacceptably costly HER electrocatalyst [9]. Thus, a number of metal oxides [10], nitrides [11], phosphides [12] have been studied. It has been found that transition metal sulphides, including sulphides of cobalt, nickel, molybdenum or copper, can demonstrate improved electrochemical performance with a combination of low cost precursors and simple fabrication techniques. Among others, cobalt sulphide (Co–S) was identified as a promising material for dye-sensitized solar cells (DSSC) or active electrocatalyst for photoelectrochemical hydrogen generation in aqueous solutions [8, 13-16]. Various fabrication techniques were studied to prepare Co–S electrode. For example, Gratzel et al. [13] have proposed electrochemical deposition method of Co–S in an alkaline cobalt-base deposition bath and employed it in DSSCs

---

\*Corresponding author: eugenijus.valatka@ktu.lt

as a counter electrode. Some other published Co–S preparation methods include the combination of electrophoretic (EPD) and ion exchange (IED) depositions techniques [17], solvothermal [7], chemical bath [18] and SILAR [19] methods.

The aim of this work was to form cobalt–sulphide films on FTO glass substrate using electrochemical deposition method and to study their structure and electrocatalytic activity in aqueous neutral solutions.

## 2. Experimental

### 2.1. Preparation of cobalt–sulphide films

Potentiodynamic electrochemical technique was employed to deposit cobalt–sulphide (denoted as Co–S throughout the paper) films on FTO glass substrate. Prior to deposition, fluorine–doped tin oxide (FTO) glass substrates (TEC15, 3.5 x 1 cm, 13  $\Omega$  sq<sup>-1</sup>) were cleaned consecutively using soap solution, deionized water and acetone in an ultrasonic bath. Thus prepared FTO plates were used as working electrodes in a thermostated three electrode cell with Ag, AgCl|KCl<sub>(sat)</sub> as a reference electrode and platinum wire (geometric area about 15 cm<sup>2</sup>) as a counter electrode. The working and counter compartments of the cell were separated by the frit. All three electrodes were placed in 100 mL deposition bath filled with Co–S precursors solutions and small amount of ammonia which was selected to maintain the neutral pH value of the deposition bath [20]. The Co–S electrosynthesis bath contained 0.5 M thiourea and 0.005 M CoCl<sub>2</sub>·6H<sub>2</sub>O as sulphur and cobalt precursors, respectively. Thiourea (CH<sub>4</sub>N<sub>2</sub>S,  $\geq$  99%, Sigma Aldrich), cobalt(II) chloride hexahydrate (CoCl<sub>2</sub> · 6H<sub>2</sub>O,  $\geq$  99%, Sigma Aldrich) and ammonia (solution 25% pure, VWR International) were used as supplied without further purification.

The electrodeposition of Co–S films was performed by cyclic voltammetry (CV). Various number of sweep cycles were used to form Co–S films while potential was cycled from -1.2 V to 0.2 V vs. Ag/AgCl at a scan rate of 5 mV s<sup>-1</sup>. During all experimental runs, the intense black films were constantly obtained as a result of electrodeposition. The as-synthesized samples were thoroughly washed with distilled water and dried at room temperature.

### 2.2. Analytical techniques

The electrochemical properties of potentiodynamically deposited Co–S samples were evaluated by computer–controlled Auto lab PGSTAT12 (Ecochemie, The Netherlands) potentiostat/galvanostat connected to a three–electrode cell. FTO/Co–S sample was used as the working electrode, platinum wire as the counter electrode and Ag, AgCl|KCl<sub>(sat)</sub> as a reference electrode. All of the electrochemical tests were performed in 1 M potassium phosphate buffer solution (pH 7).

Examination of the surface morphology and elemental composition of FTO/Co–S samples was performed using Quanta FEG 200 (FEI) high resolution scanning electron microscope (SEM) equipped with detector (Bruker AXS) for high resolution energy dispersive X-ray spectroscopy (EDX).

X-ray diffraction (XRD) patterns were recorded on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with CuK  $\alpha$  radiation. The specimens of cobalt–sulphide were scanned over the range of  $2\theta = 5\text{--}70^\circ$  at a scanning speed of 6°min<sup>-1</sup> using a coupled two theta/theta scan type.

Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Perkin Elmer FT-IR Spectrum X System. KBr was used to pellet the samples and the scans were operated in 400–4000 cm<sup>-1</sup> scanning range.

UV-Vis diffuse reflectance (UV-Vis DR) spectra of the samples were recorded on a Lambda 35 UV-Vis spectrometer (Perkin Elmer Instruments Co. Ltd., USA) equipped with a 50-mm machined Spectralon® integrating sphere. A BaSO<sub>4</sub> disc was employed as a reference. The scan ranged from 200 to 800 nm.

### 3. Results and discussion

#### 3.1. Structure and morphology of Co–S films

The obtained experimental results confirmed the possibility to form Co–S films onto FTO substrate by varying the number of CV sweep cycles in a precursor electrolyte solution. 1, 3 and 5 continuous sweep cycles were applied to form homogeneous, intensive black appearance Co–S films. An acceleration of the deposition process was observed when the temperature of the deposition bath was raised from 20°C to 50°C degrees (Fig. 1).

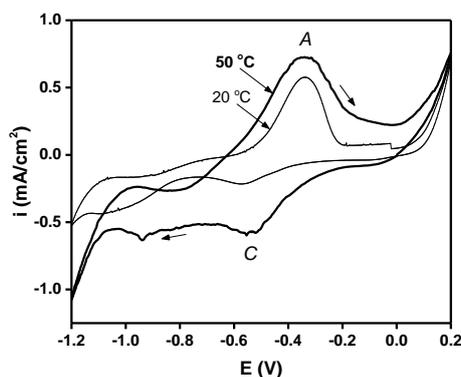


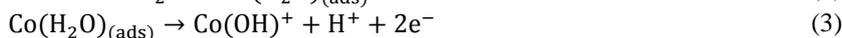
Fig. 1. Characteristic cyclic voltammograms of FTO electrode in the electrolysis bath containing 0.5 M thiourea and 0.005 M CoCl<sub>2</sub> at a scan rate of 5 mV s<sup>-1</sup>. Plot contains only the 3<sup>rd</sup> sweep-cycles

Fig. 1 demonstrates the third sweep-cycle of Co–S electrodeposition at various temperatures. Independently of the electrolysis temperature, characteristic pair of oxidation/reduction peaks (denoted as A and C) was observed at -0.34 V and -0.57 V vs. Ag/AgCl, respectively. As it is seen, the current density of the characteristic peaks significantly increased as the temperature of electrolysis bath was raised. It was observed that the thicker films can be obtained at higher temperatures. However, it should be emphasized that the quality of Co–S films deposited at 50°C was poorer, as they became cracked, less adhesive to the FTO surface and had a tendency to peel off to the solution. For this reason, our subsequent research has been mostly focused on the characterization of Co–S films electrodeposited at 20°C.

The presence of peaks A and C are in a good agreement with theoretical basis for electrochemical formation of cobalt sulphide films during electrolysis [16]. Intensive anodic peak A can be associated with the presence of Co(OH)<sub>2</sub> species on FTO surface [21]:



Moreover, this anodic peak can be partly related to the formation of a duplex passive film according to the following mechanism [22]:

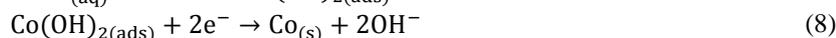


In addition, the one-electron electrochemical oxidation of the thiourea (TU) to formamidine disulphide can take place in this potential region [20].

The cathodic area (the peak C) of sweep cycles should be a result of the reduction of formed cobalt and thiourea complexes to cobalt–sulphide compounds [16]:



The nucleation and electrodeposition of metallic Co can occur at negative potentials[21]:



The increase in cathodic current at potentials more negative than -0.8 V can be attributed to the hydrogen evolution reaction:



X-ray diffraction analysis was employed to study the structure of the prepared Co–S films on FTO substrate. Fig. 2 illustrates XRD patterns obtained for Co–S films electrodeposited after 3 cycles at various temperatures. The observed halo around  $2\Theta = 10^\circ$  and the absence of characteristic diffraction peaks for crystalline cobalt sulphide suggests the existence of amorphous phase. Independently of electrodeposition temperature, no additional peaks occurred in comparison to bare FTO substrate. Due to the poor crystallinity and low amount of the deposits, the same characteristic peaks corresponding to the standard of  $\text{SnO}_2$  (PDF 46–1088) and deriving from FTO substrate can be detected in all patterns. It is interesting to note that the same XRD pattern has been observed for Co–S films annealed at  $700^\circ\text{C}$  under argon atmosphere [8]. These findings indicate the lack of significant long-range crystalline order. A more detailed *operando* analysis by Raman and X-ray absorption spectroscopy revealed that the as-deposited Co–S films can be composed of small clusters in which the cobalt is surrounded by both sulphur and oxygen [9].

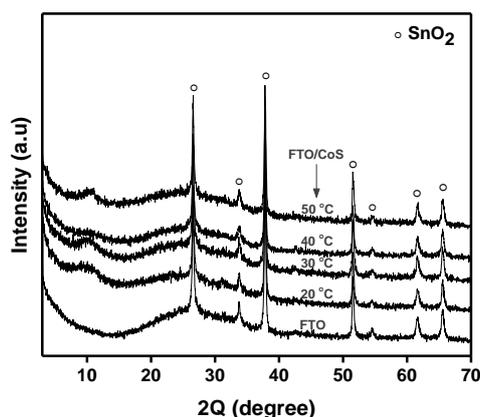


Fig. 2. X-ray diffraction patterns of bare FTO substrate and FTO/Co–S films electrodeposited at various temperatures

FT–IR spectrum of Co–S sample prepared after 3 deposition sweep–cycles is given in Fig. 3. The absorption peaks at wavenumbers  $3424\text{ cm}^{-1}$  and  $1629\text{ cm}^{-1}$  correspond to O–H stretching and bending vibrations, respectively. Furthermore, oxygen-rich samples may lead to the formation of oxo-intermediates. A series of absorption in the range of  $600\text{--}1500\text{ cm}^{-1}$  can be assigned to the various S–O bond vibrations [23]. However, the characteristic Co–O peaks were not detected. An intense absorption peak at around  $450\text{ cm}^{-1}$  can be assigned to Co–S stretching vibrations. The IR data suggest the formation of inorganic films as the characteristic peaks of thiourea functional groups [24, 25] are absent in all prepared samples.

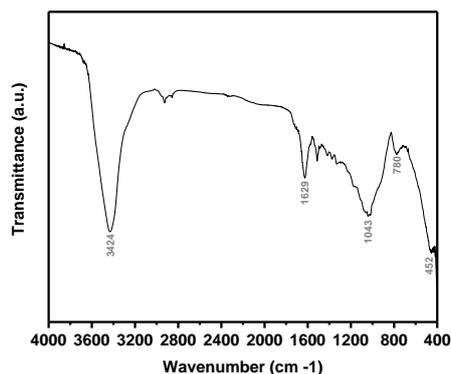


Fig. 3. Characteristic FT-IR spectrum of Co-S film electrodeposited after 3 sweep-cycles

As the number of CV cycles increases, a thicker Co-S film is electrodeposited on FTO substrate; consequently, the reduced reflectance in the visible light range occurs, as it is confirmed by UV-Vis diffuse reflectance analysis (Fig. 4).

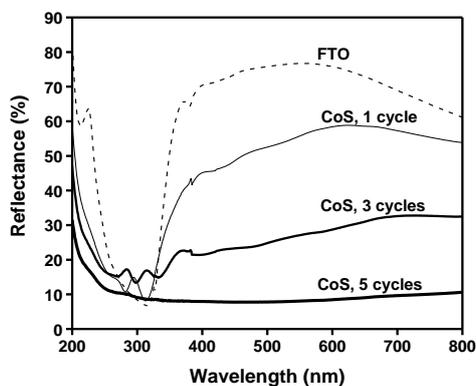


Fig. 4. UV-Vis diffuse reflectance spectra of bare FTO substrate and FTO/Co-S films formed after various deposition cycles

The correlation between morphology and deposition conditions of Co-S films is illustrated in Fig. 5. The dense layer formation of Co-S particles was detected after one-sweep-cycle deposition (Fig. 5a). It was determined that the multi-layer porous surfaces were formed with the increase of deposition sweep-cycles (Fig. 5 b, c). Fig. 5 b illustrates a honeycomb-like structure with holes and folds generally associated with higher surface roughness. The layer of folds became more uniform and the deep network-like structure was observed when the deposition was performed under five-sweep-cycles conditions (Fig. 5 c). It is known that the high surface roughness and specific surface area with holes and deep-spaced formation are favourable factors in order to enhance the access of an active sites and, therefore, electrocatalytic activity of electrode [7, 17].

Energy dispersive X-ray spectroscopy (EDX) with elemental mapping was further employed to confirm the presence of Co and S in the prepared films (Fig. 5 d). The distribution of Co and S demonstrates the network-like structure and the uniform elemental deposition after the 3<sup>rd</sup> sweep-cycle.

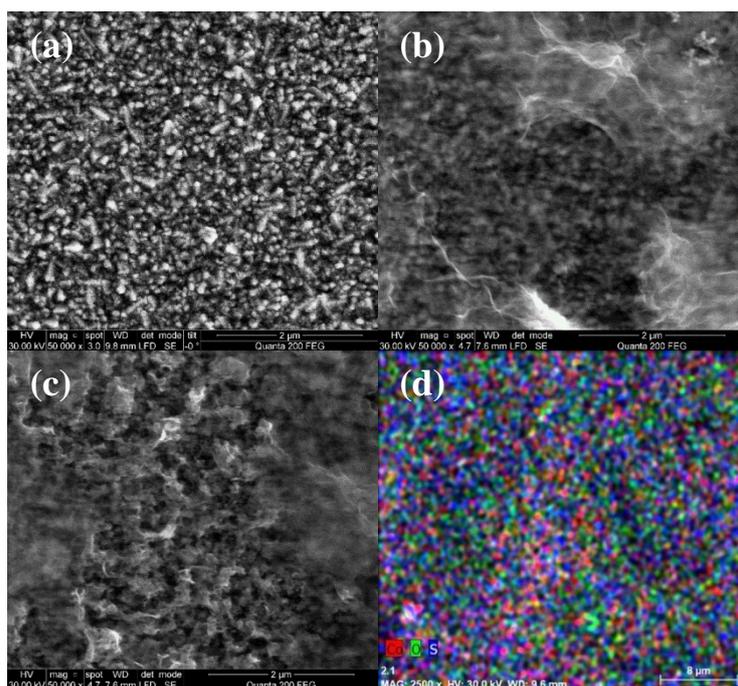


Fig. 5. SEM images of FTO/Co-S films after 1 (a), 3 (b) and 5 (c) deposition cycles at  $\times 50\,000$  magnification and EDX elemental mapping of three-sweep-cycle Co-S film (d)

It should, however, be noted that a high content of oxygen was constantly detected in Co-S samples and it can be explained by the next three reasons. Firstly, some amount of silica and tin oxide from the FTO substrate was identified via EDX analysis (Fig. 6). Secondly, the oxide/hydroxide fraction in the film, probably, derived from electrodeposition mechanism described earlier. Usually, electrodeposited cobalt compounds are known to be covered by a native passive film of  $\text{CoO}/\text{Co}(\text{OH})_2$  and even undergo further oxidation to  $\text{Co}(\text{III})$  oxidized compounds depending on pH value of the deposition bath, the charge transfer number and applied potential [16, 22, 26]. And finally, air exposure might be powerful oxidizer of porous Co-S film surface. A considerable change of Co/S ratio was observed during the increase of the Co-S deposition sweep-cycles (Table 1). For example, the ratio of Co/S was increased from 2.4/1 to 1/1 when the deposition was varied from one to three-sweep-cycles, respectively. EDX spectra further illustrate the elemental composition of 1, 3 and 5-sweep-cycled Co-S samples and are shown in Figure 6. Sn and Si were detected as they originate from FTO substrate and the intensity of these background elements tends to reduce as a result of increased number of sweep-cycles.

Table 1. EDX data of Co-S films synthesized after 1, 3 and 5 CV deposition cycles

Element	Quantity (at., %) after 1 CV	Quantity (at. %) after 3 CV	Quantity (at. %) after 5 CV
Cobalt	0.11	0.54	2.42
Sulphur	0.044	0.52	1.93
Oxygen	84.99	86.49	80.81

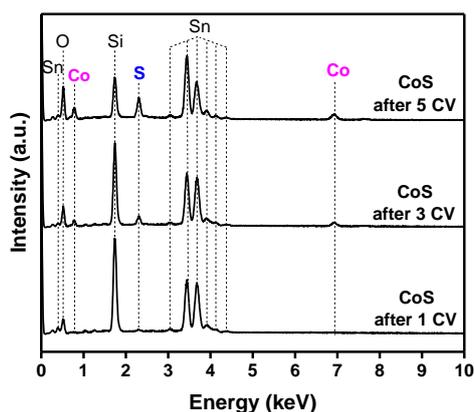


Fig. 6. EDX spectra of Co-S films prepared after 1, 3 and 5 CV deposition cycles

### 3.2. Electrochemical performance of Co-S films

Electrocatalytic behaviour of the FTO/Co-S electrodes were evaluated under polarization in 1 M phosphate buffer solution. Polarization curves of bare FTO substrate and 1, 3 and 5-sweep-cycled Co-S samples are presented in Fig. 7. A relatively low scan rate was used to utilize layered honeycomb-like structure for charge migration in whole surface areas [26]. It can be observed that the presence of Co-S significantly improves the catalytic behaviour of bare FTO substrate under HER conditions and current density tends to increase with the increase in the number of deposition sweep-cycles. The results of *operando* spectroscopic analysis of amorphous Co-S catalyst in electrochemical hydrogen evolution reaction suggest that the Co-S is spontaneously transforming into  $\text{CoS}_2$ -like molecular clusters under cathodic polarization [9]. It has been estimated that Co-S electrocatalyst can contain roughly 60% CoO and 40% CoS in the dry state and 26% CoO and 74% CoS under HER conditions.

The collected current-potential data was used for the determination of Tafel slope  $b$  [27]. This parameter is of fundamental importance as it is an indicative parameter of the electrode reaction mechanism. The inset of Figure 7 presents the dependence of potential as a function of logarithm of the current density for 5 sweep-cycled electrodes. The change in the values of Tafel slope can be considered as an indication of the change of the rate limiting step. It can be observed that the Tafel slope values (46 and 122 mV, respectively) are in good agreement with generally accepted Tafel slopes for HER on platinum (29, 38 or 116 mV [28]).

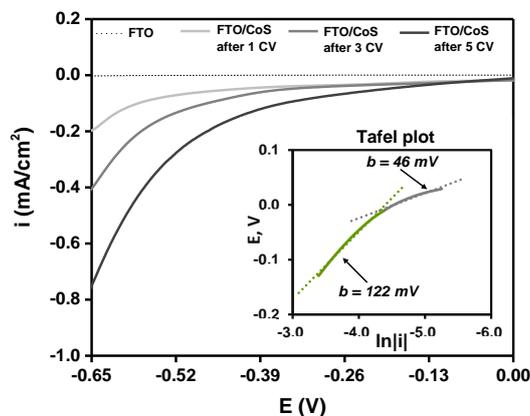


Fig. 7. Polarization curves of bare FTO and freshly prepared FTO/Co-S electrodes in 1.0 M phosphate buffer solution (pH 7) at a scan rate of  $5\text{ mV s}^{-1}$ . Inset: Tafel plot of FTO/Co-S electrode prepared after 5 deposition cycles

As the stability is one of the most important characteristics of HER electrodes, the behaviour of Co–S films was evaluated under controlled potential electrolysis (Fig. 8). The results of chronoamperometry tests revealed stable but relatively small current density values of FTO/Co–S electrodes at +0.01 V potential. However, when the amount of Co–S was increased via sweep-cycles and raised from 1 CV to 5 CV, the steady-state current density was found to increase in double. More detailed structural and electrochemical characterization of as-deposited Co–S films is currently under investigation and will be published in separate paper.

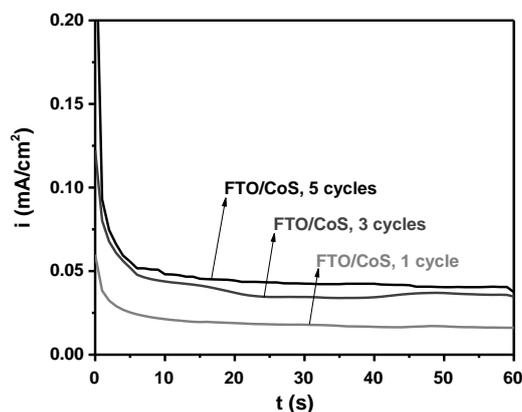


Fig. 8. Characteristic chronoamperograms of freshly prepared FTO/Co–S electrodes at +0.01 V in 1 M phosphate buffer solution (pH 7)

#### 4. Conclusions

Potentiodynamic electrochemical deposition technique was applied for the synthesis of cobalt–sulphide (Co–S) films on FTO substrate. It was established that the electrodeposition in the range of 20–50°C leads to the formation of amorphous Co–S films, as it is evidenced by XRD results. SEM-EDX analysis revealed the honeycomb structure accompanied with 1/1.2 ratio of Co/S in as-deposited films. It is possible to control the amount of Co–S deposits on FTO surface by varying the number of deposition cycles. The study of electrochemical behaviour of as-deposited Co–S films showed a possibility to use them as an efficient electrocatalyst in electrochemical water splitting. The films exhibit low over potential with a Tafel slope of 122 mV decade<sup>-1</sup>.

#### References

- [1] Y. Liu, Y. Li, H. Kang, T. Jin, L. Jiao, *Mater. Horiz.***3**,402 (2016).
- [2] X. Rui, H. Tan, Q. Yan, *Nanoscale***6**,9889 (2014).
- [3] M.-R. Gao, Y.-F. Xu, J. Jiang, S.-H. Yu, *Chem. Soc. Rev.***42**, 2986 (2013).
- [4] X. Li, X. Hao, A. Abudula, G. Guan, *J. Mater. Chem. A***4**, 11973 (2016).
- [5] M.S. Faber, S. Jin, *Energy Environ. Sci.*, **7**, 3519 (2014).
- [6] K. Rajeshwar, R. McConnell, S.E. Licht, *Solar Hydrogen Generation*, Springer, New York (2008).
- [7] L. Zheng, X. Sun, L. Chen, C. Bao, W. Luo, N. Huang, P. Sun, Y. Sun, L. Fang, L. Wang, *J. Mater. Sci.***51**, 4150 (2016).
- [8] Y. Sun, C. Liu, D.C. Grauer, J. Yano, J.R. Long, P. Yang, C.J. Chang, *J. Am. Chem. Soc.* **135** (47),17699 (2013).
- [9] N. Kornienko, J. Resasco, N. Becknell, C.-M. Jiang, Y.-S. Liu, K. Nie, X. Sun, J. Guo, S.R. Leone, P. Yang, *J. Am. Chem. Soc.***137** (23),7448 (2015).
- [10] N.V. Lapin, N.Y. D'yankova, *Inorg. Mater.***49**,975 (2013).
- [11] G.R. Li, J. Song, G.L. Pan, X.P. Gao, *Energy Environ. Sci.***4**, 1680 (2011).

- [12] E.J. Popczun, J.R. McKone, C.G. Read, A.J. Biacchi, A.M. Wiltrout, N.S. Lewis, R.E. Schaak, *J. Am. Chem. Soc.* **135**(25),9267 (2013).
- [13] M. Wang, A.M. Anghel, B. Marsan, N.-L. Cevey Ha, N. Pootrakulchote, S.M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **131** (44), 15976 (2009).
- [14] S.K. Swami, N. Chaturvedi, A. Kumar, R. Kapoor, V. Dutta, J. Frey, T. Moehl, M. Grätzel S. Mathew, M.K. Nazeeruddin, *J. Power Sources*, **275**, 80 (2015).
- [15] J.Y. Lin, J.H. Liao, T.C. Wei, *Electrochem. Solid-State Lett.* **14**, D41 (2011).
- [16] J.Y. Lin, J.H. Liao, S.W. Chou, *Electrochim. Acta* **56**, 8818 (2011).
- [17] J. Huo, M. Zheng, Y. Tu, J. Wu, L. Hu, S. Dai, *Electrochim. Acta*, **159**,166 (2015).
- [18] H.-J. Kim, S.-W. Kim, C.V.V.M. Gopi, S.-K. Kim, S.S. Rao, M.-S. Jeong, *J. Power Sources* **268**,163 (2014).
- [19] Y. Shengyuan, A.S. Nair, Z. Peining, S. Ramakrishna, *Mater. Lett.* **76**,43 (2012).
- [20] J. Huo, J. Wu, M. Zheng, Y. Tu, Z. Lan, *Electrochim. Acta* **180**, 574 (2015).
- [21] J.S. Santos, R. Matos, F. Trivinho-Strixino, E.C. Pereira, *Electrochim. Acta* **53**, 644 (2007).
- [22] W.A. Badawy, F.M. Al-Kharafi, J.R. Al-Ajmi, *J. Appl. Electrochem.* **30**,693 (2000).
- [23] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A: Theory and Applications in Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn (1997).
- [24] G. Rajadurai, A. Puhaj Raj, S. Pari, *Arch. Phy. Res.* **4**, 61 (2013).
- [25] V. Kumar, R. Sundararajan, *J. Miner. Mater. Charact. Eng.* **3**,118 (2015).
- [26] R.S. Ray, B. Sarma, A.L. Jurovitzki, M. Misra, *Chem. Eng. J.* **260**, 671 (2015).
- [27] J.M. Falkowski, Y. Surendranath, *ACS Catal.* **5** (6),341 (2015).
- [28] J.O.M. Bockris, E.C. Potter, *J. Electrochem. Soc.* **99** (4), 169 (1952).