

Gas diffusion electrodes (GDEs) with Ag/ γ -MnO₂ bimetallic catalytic composition for metal hydride/air batteries

B. Abrashev*, V. Terziev, D. Paskalev, E. Lefterova, M. Dimitrova, O. Dimitrov, A. Gigova, K. Petrov

Acad. E. Budevski Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 10, 1113 Sofia, Bulgaria

Received: November 25, 2022; Accepted: March 08, 2023

The gas diffusion electrode (GDE) consists of a carbon-based gas diffusion layer (GDL) and an active layer (AL). In this study GDE with bimetallic AL containing Ag/ γ -MnO₂ was investigated and compared with previously optimized GDE with Ag/Co₃O₄ composition. The catalytic structure was created by depositing of a mixture of catalysts containing γ -MnO₂ and Ag with a weight ratio between the two components of 1:1. The prepared electrodes were examined before and after work by XRD phase analysis. The morphology of the above-studied ALs and GDL was investigated with scanning electron microscopy (SEM) and BET analysis, respectively. The polarization, charge/discharge tests and impedance analysis were carried out in a half-cell configuration in 6M KOH. Long-term tests of the two GDEs showed good mechanical and electrochemical stability of over 300-500 charge/discharge cycles.

Keywords: gas diffusion electrode, bimetallic catalyst, carbon-based electrodes

INTRODUCTION

The rise in the price of electricity affects both the quality of life and the development of every sphere of the global economy. Furthermore, the constant growing need for energy in order to meet the increasing demand leads to environmental concerns. A transition to clean energy sources/renewable energy sources (RES) could help reduce the reliance on fossil fuels but in that case energy storage arises as a potential challenge for sustainability due to their intermittent character [1]. There is quite a variety of solutions for rechargeable batteries to store and release high amounts of energy in a short time when required such as: metal/air [2-4], nickel/metal hydride [5], etc. For instance, rechargeable metal hydride (MH)/air batteries are envisaged as very promising battery systems with long cycle life, possessing a high capacity. They are very appropriate for stationary applications – one of which is storing energy from RES. Another advantage of metal hydride/air systems is that they can operate in an open-air atmosphere and strong alkaline media [6-8]. A key matter in this type of batteries is the development of the bifunctional GDE which is responsible for both the oxygen reduction reaction (ORR, discharge process) and the oxygen evolution reaction (OER, charge process). Technically, GDEs can have different types of catalysts, including metal, non-metal and molecular catalysts, as well as enzymes and microbes [9].

Electrocatalysts able to sustain both oxygen

reduction and oxygen evolution at high current densities are essential components of metal hydride/air secondary batteries. The most suitable electrocatalysts for ORR in alkaline media are platinum and its compounds/derivatives while IrO₂ and RuO₂ are suitable for the OER [10]. In fact, because of their high price, substitutes are sought so as to replace these materials. For the OER metal oxides with spinel structure are highly appropriate. The spinels have been broadly used as bifunctional oxygen electrocatalysts in alkaline media but their performance at practical current densities has been rarely reported. One of the reasons for that matter is that in order to operate as a bifunctional electrode at high current densities, the electrocatalyst should be placed into a GDE structure that allows a high flux of O₂ to the catalyst sites during battery discharge and effective removal of O₂ away from these sites during battery charge. Manganese has multiple crystallographic phases with different physical and chemical properties and one of its most stable forms is MnO₂. Generally, MnO₂ can exist in a number of phase structures such as α , β , γ , δ , ϵ , λ and so on [11-13]. In the current investigation the focus was on γ -MnO₂ as a catalyst for the OER due to its spinal structure. Another widely used catalyst for the OER is cobalt oxide [14]. The activity of the cobalt-based catalyst for the OER depends on the different oxidation states of cobalt (Co^{II}, Co^{III} and Co^{IV}) at the surfaces of the electrocatalysts [15, 16]. A commonly used catalyst mainly for the ORR is Ag. ORR mechanism in alkaline media may be

* To whom all correspondence should be sent:
E-mail: babrashev@iees.bas.bg

classified through two pathways, i. e. direct four-electron pathway and two-electron pathway. For the first pathway, one oxygen molecule receives 4e⁻ and is reduced to 4OH⁻. For the second pathway, the oxygen molecule is firstly reduced to o H₂O₂ or HO₂⁻ intermediate, then the intermediate transfers into electrolyte or is further reduced to OH⁻ *via* receiving 2e⁻ (indirect four-electron pathway) [17]. The silver in the general case catalyzes the direct 4e⁻ reaction pathway and also the HO₂⁻ anion disproportionation, being cheaper in comparison to conventional precious metal catalysts such as Pt, Au and Pd [18].

In our study we built the AL of the GDE using bimetallic catalysts and Teflon as a binder. For the gas diffusion layer, we applied teflonized carbon black and used a technology developed in IEEs-BAS [19]. The aim of this study is to show the advantages of two of the most widely used electrocatalysts (γ -MnO₂ and Ag) in operation as bifunctional catalysts for ORR and OER. The obtained results were compared with the GDE with same GDL and different AL (Co₃O₄ and Ag). The focus of the current investigation is the influence of different catalysts on the electrochemical properties of GDE. Moreover, the varying ratio between the catalysts and their particle size is also studied.

EXPERIMENTAL

Electrode preparation

The GDL for both investigated GDEs was produced from Vulcan XC-72 R (Cabot corp., 30 nm particle size) which was modified by polytetrafluoroethylene (PTFE) (60 wt % dispersion in H₂O, 0.05-0.5 μ m, Sigma Aldrich). The carbon blacks were teflonized up to 60 wt%. GDL was applied in a pressform completely covering its inner surface. The relative density of the layer was 50 mg.cm⁻². The AL was applied on the tightly placed GDL. It contains a bifunctional catalyst and 10 wt.% PTFE (10 μ m particle size) powder (Sigma Aldrich), taken per the mass of catalysts. The bifunctional catalyst was composed, in one case of Co₃O₄ (Sigma Aldrich), particle size <50 nm + Ag (Ferro AG), particle size 4-30 μ m (30:70 wt.%) [19] and in the other case, after ratio optimization of γ -MnO₂ (EMD), particle size 40 μ m and the same Ag (50:50 wt.%). The working area of the GDEs was 10 cm². The relative density of this layer is 40 mg.cm⁻², where the GDL was again applied by sealing the inner area of the pressform. A stainless steel mesh (Hebei Standard Filter Equipment), mesh count 100 was placed on top of the AL for the current collector.

Pressure of 300 kg.cm⁻² was applied to the pressform for 3 minutes at 300°C.

Experimental conditions

The charge/discharge tests were conducted using a six-channel Galvanostat 54 (PMC) testing system. The cell discharge was controlled by limiting time or voltage. The charge is defined by time up to 45 min and voltage limit up to +2 V and time up to 30 min and voltage limit -1 V for discharge, respectively. The polarization, charge/discharge tests and impedance analysis were carried out in a specially designed three-electrode half-cell configuration in 6M KOH - electrolyte and using reversible hydrogen electrode (RHE) (Gaskatel) for reference electrode, and stainless steel mesh as a counter electrode. The impedance measurements were conducted on GAMRY Instruments Reference 3000 potentiostat/galvanostat in a frequency range of 100 kHz to 10 mHz with ten points per decade. Sine signal of 10 mV peak to peak was applied.

RESULTS AND DISCUSSION

Structure and morphology

XRD analysis (shown on Fig. 1) reveals a mixture of Ag/Co₃O₄ and a small amount of fcc-alloy (or CoC_x) and Ag/ γ -MnO₂ for the respective catalysts. The XRD patterns do not show formation of new phases after the electrodes were used. A strong widening of the diffraction peaks of silver was observed due to the reduction in the size of the crystallites (Table 1).

The morphology of the catalysts, as well as of the GDEs prepared with them was examined using scanning electron microscopy (SEM). On Figs. 2 and 3 the microphotographs of the studied ALs of GDE at different magnifications are shown. From the SEM images in Fig. 2 it is clear how the smaller spherical Co₃O₄ particles cover the larger silver particles. At higher magnification (\times 3000 and \times 10000) a layered structure is clearly observed. In Fig. 3, in the AL prepared from a mixture of Ag/ γ -MnO₂, rough morphology and homogeneous particle distribution of the two catalysts are observed. Additionally, the smaller irregularly shaped silver particles, which are in a fairly wide range, almost completely envelop the larger particles of γ -MnO₂. The microphotographs of the different GDEs show significant differences in the particles' morphology and size as well.

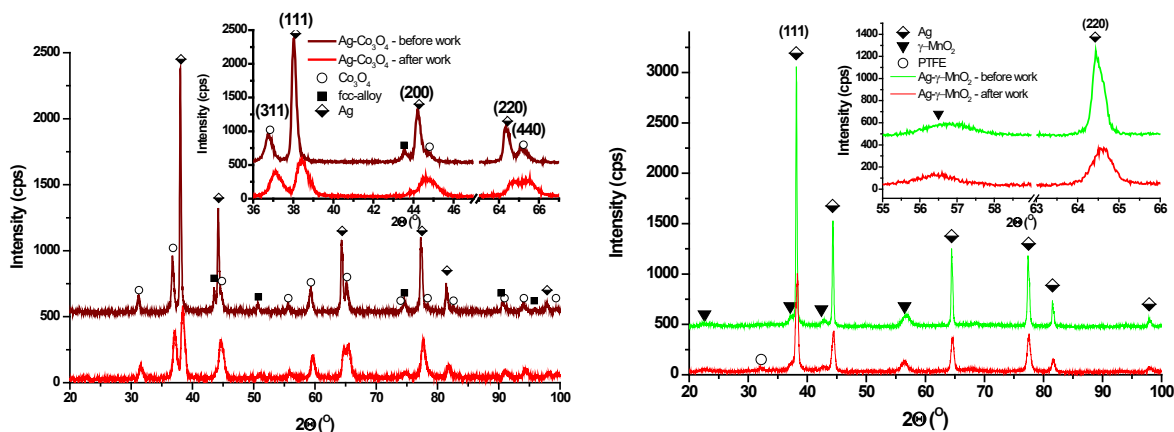


Fig. 1. XRD phase analysis of the prepared electrodes with bimetallic structure (Ag/Co₃O₄ and Ag/ γ -MnO₂) before and after work

Table 1. XRD parameters of GDEs with different AL

| | Phases | Average crystalline size, nm | |
|--|---|------------------------------|--|
| | | Ag | Co ₃ O ₄ or MnO ₂ |
| Ag-Co ₃ O ₄ -before work | Ag+Co ₃ O ₄ , fcc-alloy | 49 | 18 |
| Ag-Co ₃ O ₄ -after work | Ag+Co ₃ O ₄ , fcc-alloy | 15 | 13 |
| MnO ₂ -Ag-before work | Ag+ γ -MnO ₂ | 50 | 8 |
| MnO ₂ -Ag-after work | Ag+ γ -MnO ₂ PTFE | 18 | 8 |

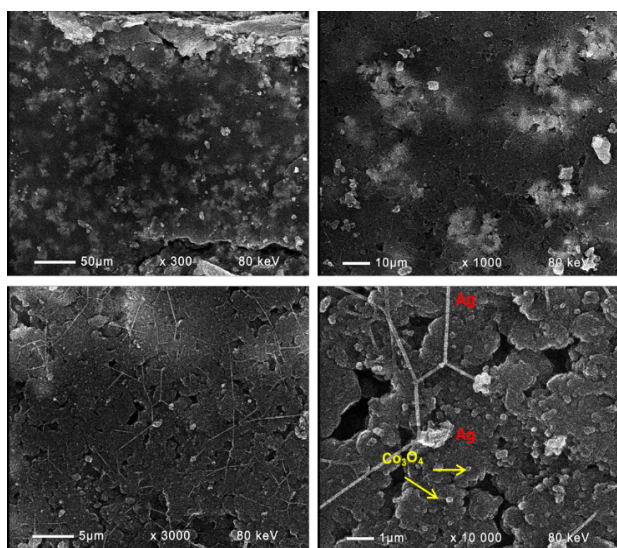


Fig. 2. SEM micrographs of GDE with bimetallic AL (Ag/Co₃O₄)

BET analysis

A study by BET analysis revealed a high specific surface area of the gas diffusion layer (GDL) in GDEs with bi-metallic catalysts in the AL. The average size of the mesopores is about 10.7 nm which is a prerequisite for the predominance of Knudsen diffusion. The presence of this type of diffusion is also a prerequisite for the fastest and most efficient access of oxygen to the catalytic

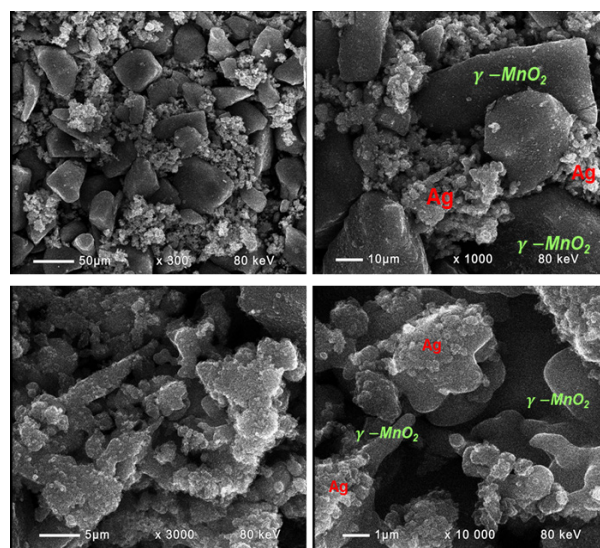


Fig. 3. SEM micrographs of GDE with bimetallic AL (Ag/ γ -MnO₂)

surface and is the reason for the high values of diffusion-limited current density i_d (for ORR). The undergoing of this type of diffusion is also one of the explanations for the good discharge characteristics of these GDEs. Moreover, the BET analysis has given another important information that the GDL has a high specific surface area of 118.8 m².g⁻¹ and total pore volume (for pores smaller than 132 nm) of 0.318 cm³.g⁻¹, which is probably another reason for the facilitated access of oxygen to the AL.

Electrochemical characterization

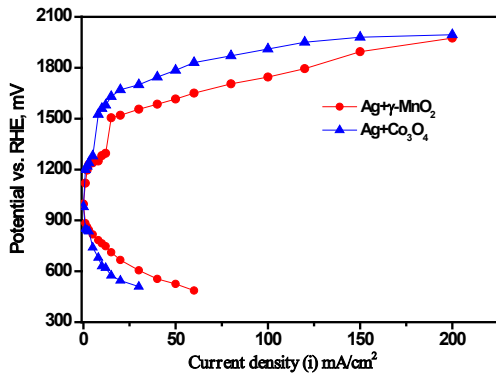


Fig. 4. Polarization curve of GDEs with different CL

On Fig. 4 the volt-ampere characteristics of the investigated GDEs are shown. It can be clearly seen that the use of the mixture Ag/Co₃O₄ for the obtaining of the AL in the GDE current density of 30 mA·cm⁻² was achieved for the ORR. With

replacement of the Co₃O₄ with γ - MnO₂ the applied current density for the electrochemical discharge considerably increases – up to 60 mA·cm⁻². Moreover, the GDE efficiency standard for OER is potential-E₁₀ [20]. For the investigated GDEs the values were E₁₀=1295 mV for Ag/Co₃O₄ AL and E₁₀= 1282 mV for Ag/ γ -MnO₂, which additionally confirmed the good electrochemical behavior of the two investigated GDEs. With the use of the two mixtures of bi-metallic catalysts a leap is observed in the interval of 1200-1550 mV in the polarization curves of the silver containing electrode. That effect was carefully studied by Amin [21] and is related to the formation of Ag₂O and/or Ag^IAg^{III}O₂ during the OER. Long-term tests of the two GDEs showed very good mechanical stability of over 300-500 charge/discharge cycles (Fig. 5a) and b)). That is also confirmed by the very smooth increase (almost insignificant) of polarization between the first and last cycle at GDE with Ag/ γ -MnO₂ structure (Fig. 5 b).

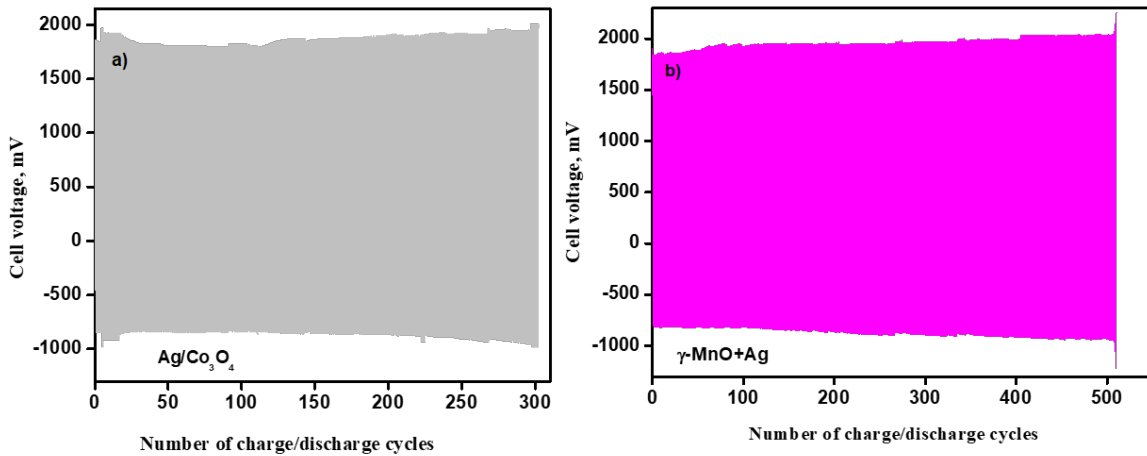


Fig. 5. Durability test of the GDEs with a) Ag/Co₃O₄ and b) Ag/ γ -MnO₂

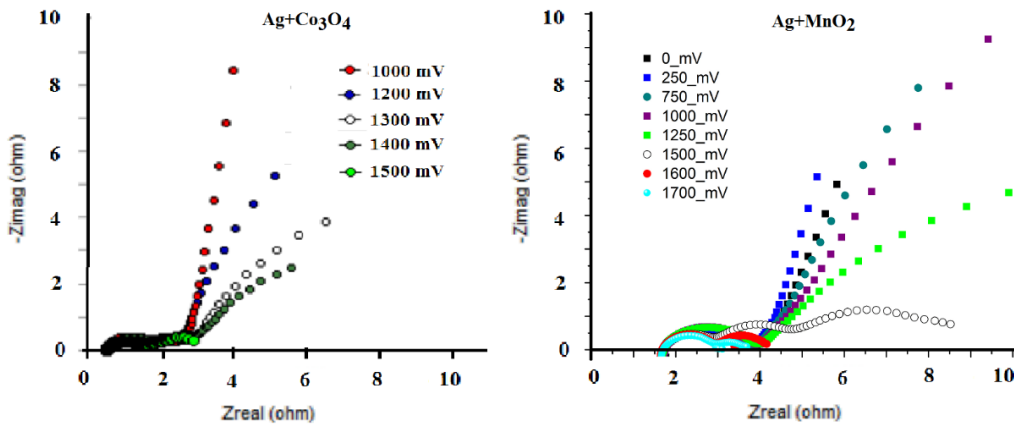


Fig. 6. Nyquist plots of impedance spectra of the GDEs with Ag/Co₃O₄ and Ag/ γ -MnO₂.

EIS investigations

Fig. 6 shows the Nyquist plots of the Ag/Co₃O₄ and Ag/ γ -MnO₂ electrodes at different potentials. From high to medium frequencies, the impedance spectra consist of partially overlapping semicircles and remain almost unchanged with increasing potential mainly due to the heterogeneous structure of the electrodes (the resistance of the pores, particles and boundaries between them) without a contribution by the electrochemical processes. Conversely, the impedance at low frequencies depends on the applied potential and reflects the electrochemical behavior of the electrodes. At lower potentials, far from the OER potential, the electrode behaves as a pseudocapacitor (slanted line) due to the formation of an electric double layer. As the potential increases, the line at low frequencies gradually bends and a new depressed semicircle with decreasing diameter is formed in a result of the OER with a decreasing charge transfer resistance (R_{ct}). At the higher potentials (over 1500 mV) R_{ct} becomes very small and the semicircle is not distinguished.

CONCLUSIONS

GDEs with different AL (Ag/Co₃O₄ and Ag/ γ -MnO₂) and same GDL were investigated with modern physical and electrochemical methods. From these studies, it was found out that the equable weight distribution of the two catalysts (1:1) with Ag/ γ -MnO₂ and their almost equal particle sizes give good results (higher than those with cobalt and silver) in the operation of the secondary GDE. Statistically, this morphology also determines a homogenous distribution of the pores (observed in the SEM microphotograph), from which it follows that the active sites for the two oxygen reactions are almost equally distributed in the volume of the catalytic layer. The EIS analysis gives the impression that the electrochemical behavior of the investigated GDEs also shows a behavior similar to that of supercapacitors. In future studies, more thorough attention will be paid to this fact.

Acknowledgements: The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Center of Competence HITMOBIL - Technologies and Systems for Generation, Storage and Consumption of Clean Energy”, funded by Operational Programme “Science and Education for Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund. This work is partially supported by the Bulgarian Ministry of Education and Science under National Roadmap for Scientific Infrastructure (CMD No. 354 of

29.06.2017) “Distributed infrastructure of centers for synthesis and characterization of new materials and conservation of archeological and ethnographic artefacts, INFRAMAT” (Contract D01-306/20.12.2021).

REFERENCES

1. B. Abrashev, M. Slavova, E. Mladenova, V. Terziev, B. Burdin, G. Raikova, K. Petrov, *Journal of Chemical Technology and Metallurgy*, **56** (6), 1261 (2021).
2. C. Wang, Y. Yu, J. Niu, Y. Liu, D. Bridges, X. Liu, J. Pooran, Y. Zhang and A. Hu, *Applied Sciences*, **9** (14), 2787 (2019).
3. J. Yi, P. Liang, X. Liu, K. Wu, Y. Liu, Y. Wang, Y. Xia, J. Zhang, *Energy Environ. Sci.*, **11**, 3075 (2018).
4. L. Yaqoob, T. Noor, N. Iqbal, *Journal of Energy Storage*, **56**, 106075 (2022).
5. M. Karwowska, T. Jaron, K. J. Fijalkowski, P. J. Leszczynski, Z. Rogulski, A. Czerwinski, *J. Power Sources*, **263**, 304 (2014).
6. Y. J. Wang, B. Fang, D. Zhang, A. Li, D. P. Wilkinson, A. Ignaszak, L. Zhang, J. Zhang, *Electrochem. Energy Reviews*, **1**, 1 (2018).
7. A. G. Olabi, E. T. Sayed, T. Wilberforce, A. Jamal, A. H. Alami, K. Elsaid, S. M. A. Rahman, S. K. Shah, M. A. A., *Energies*, **14**, 7373 (2021).
8. H. Aldave, E. Andreoli, *Catalysts*, **10**, 713 (2020).
9. R. Ponnusamy, R. Venkatesanb, M. Kandasamy, B. Chakraborty, C. S. Routa, *App. Surface Science*, **487**, 1033 (2019).
10. J. Zhang, Q. Zhou, Y. Tang, L. Zhang, Y. Li, *Chem. Sci.*, **10**, 8924 (2019).
11. H. Radinger, P. Connor, R. Stark, W. Jaegermann, B. Kaiser, *Chem. Cat. Chem.*, **13**, 1175 (2021).
12. S. Dey, V. V. P. Kumar, *Current Research in Green and Sustainable Chemistry*, **3**, 100012 (2020).
13. D. Pletcher, X. Li, S. W. T. Price, A. E. Russell, T. Sönmez, S. J. Thompson, *Electrochim. Acta*, **188**, 286 (2016).
14. J. Shin, J. K. Seo, R. Yaylian, A. Huang, Y. S. Meng, *International Materials Reviews*, **65**, 6 (2020).
15. X. He, F. Yin, G. Li, *Int. J. Hydrog. Energy*, **40**, 9713 (2015).
16. H. Osgood, S. V. Devaguptapu, H. Xu, J. Cho, G. Wu, *Nano Today*, **11**, 601 (2016).
17. Q. Liu, Z. Pan, E. Wang, L. An, G. Sun, *Energy Storage Materials*, **27**, 478 (2020).
18. F. W. T. Goh, Z. Liu, X. Ge, Y. Zong, G. Du, T. S. A. Hor, *Electrochim. Acta*, **114**, 598 (2013).
19. B. Abrashev, D. Uzun, A. Kube, N. Wagner, K. Petrov, *Bulg. Chem. Comm.*, **52** (2), 245 (2020).
20. M. Tahira, L. Pana, F. Idreesd, X. Zhanga, L. Wanga, J. J. Zoua, Z. L. Wangb, *Nano Energy*, **37**, 136 (2017).
21. H. M. A. Amin, H. Baltruschat, D. Wittmaier, K. A. Friedrich, *Electrochim. Acta*, **151**, 332 (2015).