Study of the Oxygen Evolution Reaction at Strontium Palladium Perovskite Electrocatalyst in Acidic Medium

Areej A. Eskandrani 1, Shimaa M. Ali 1,2,* and Hiba M. Al-Otaibi 1

1 Department of Chemistry, Faculty of Science, Taibah University, Madinah 3002, Saudi; a.eskandrani@gmail.com (A.A.E.); black.cat1900@hotmail.com (H.M.A.-O.)
2 Department of Chemistry, Faculty of Science, Cairo University, Giza 12613, Egypt
* Correspondence: sali@sci.cu.edu.eg or dr_shimaaali80@yahoo.com

Received: 2 May 2020; Accepted: 18 May 2020; Published: 27 May 2020

Abstract: The catalytic activity of SrPdO3, prepared through the sol-gel citrate-combustion method for the oxygen evolution reaction (OER) in a 0.1 M HClO4 solution, was investigated. The electrocatalytic activity of SrPdO3 toward OER was assessed via the anodic potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The glassy carbon modified SrPdO3 (GC/SrPdO3) electrode exhibited a higher electrocatalytic activity, by about 50 times, in comparison to the unmodified electrode. The order of the reaction was close to unity, which indicates that the adsorption of the hydroxyl groups is a fast step. The calculated activation energy was 21.6 kJ.mol$^{-1}$, which can be considered a low value in evaluation with those of the reported OER electrocatalysts. The SrPdO3 perovskite portrayed a high catalyst stability without any probability of catalyst poisoning. These results encourage the use of SrPdO3 as a candidate electrocatalyst for water splitting reactions.

Keywords: perovskite; SrPdO3; catalyst; OER; electrochemical techniques

1. Introduction

Electrochemical water splitting is the process of the decomposition of water into its components, hydrogen and oxygen, by applying an electric current in the presence of an electrolyte. It provides a green alternative route for producing hydrogen fuel, which can be utilized instead of non-renewable and environmentally harmful fossil fuels [1–4]. The oxygen evolution reaction (OER) and the anodic reaction of the water splitting process are the major challenges facing researchers. The kinetics of the OER involve complicated multi-electron steps with the prospective existence of several accompanying processes such as the dissolution of the metal oxide catalyst. Thus, the multitude and complexity of the OER mechanism can create difficulty in comprehending it clearly [5,6]. In addition, the OER requires the application of high overpotentials [7–9], leading to a decrease in the efficiency of the hydrogen production by the water splitting. The most common catalysts for the OER are IrO2/RuO2, Pt, and HfN which can be efficiently employed but with low stability and high cost [10,11]. Nowadays, researchers seek multi-functional catalysts, which are abundant, cost-effective, stable, and of high catalytic activity. Perovskites, mixed metal oxides possessing the general formula ABO3 where A is a lanthanide and B is a transition metal, have been extensively used as effectual catalysts for OER in alkaline [12–19] and acidic media [20–24]. Lu and co-workers have reported that the LaCoO3 perovskite demonstrated high electrocatalytic behavior due to its unique electronic structure, which facilitates the presence of the oxygen vacancies in a high concentration [25]. Oxygen vacancies can highly increase the intrinsic activity of the perovskite active sites for the electro-oxidation reactions [26–31].
The SrPdO₃ perovskite, prepared for the first time by the citrate combustion methodology by our group, presented interesting electrocatalytic and sensing applications [32]. Furthermore, SrPdO₃ has been used as an efficient catalyst for the hydrogen evolution reaction [32], which was subsequently implemented for the first time by our group as an electrochemical sensor for several neurotransmitters and hydrazine detection [33–35]. It was discovered that the nano-dispersed Pd sites within the stable perovskite matrix are more effectual than the electro-deposited Pd. Recently, the JCPDS card of the SrPdO₃ perovskite (00-025-0908) has been replaced by the JCPDS card of Sr₂PdO₃ (00-028-1249). It was reported that the partial substitution at the A-site of Sr₂PdO₃ and the formation of the nano-composites of the Sr₂PdO₃/carbon nanotubes and Sr₂PdO₃/gold nanoparticles can further enhance its electro-sensing ability for glucose and some drugs [36–38]. The study of the electronic structure of SrPdO₃ disclosed that it can exhibit a spin transition from low to high at a certain temperature, which is similar to the isoelectronic LaCoO₃ [39], and is one of the main reasons for the enhanced electrocatalytic activity of LaCoO₃ for the OER.

In this work, Sr₂PdO₃, prepared by the sol-gel citrate-nitrate combustion procedure, was employed as an electrocatalyst for the OER in an acidic medium. The electrocatalytic activity was examined by the potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS). The kinetic and thermodynamic evaluations were performed to identify the reaction order and the activation energy, respectively. The catalyst stability was also investigated to ensure a satisfactory performance.

2. Results and Discussion

2.1. Structural and Surface Characterizations of Sr₂PdO₃

Figure 1A illustrates the XRD spectrum of the strontium palladium perovskite, prepared by the citrate-combustion method at a pH value of 2 and at a calcination temperature of 750 °C for 3 h. The formation of the orthorhombic Sr₂PdO₃ perovskite is confirmed by the appearance of its theoretical major peak (110), JCPDS card number: 00-028-1249. However, the major phase of the fashioned sample is SrPd₃O₄, which is verified via the XRD pattern, displays a major peak at (210), and agrees with the theoretical value, Figure 1A. The formation of SrPd₃O₄ as a secondary phase, during the synthesis of Sr₂PdO₃, is well reported, due to the self-regeneration property of the Pd-based perovskites [40]. However, in the prepared sample, SrPd₃O₄ is the major phase; this is possibly because of the use of Pd⁴⁺ rather than the Pd²⁺ salt as a precursor during the synthesis. The calculated average particle size, according to the Scherrer equation [41], is 24.2 nm. The value of the measured BET surface area is 5.0 m² g⁻¹.
Figure 1. The (A) XRD pattern and (B) TEM image of Sr$_2$PdO$_3$ prepared by the citrate-method, miller indices (h, l, k) are showed.

The morphology of the prepared Sr$_2$PdO$_3$ is observed by the TEM, Figure 1B. It is witnessed that the prepared perovskites consist of agglomerations of orthorhombic particles.

2.2. Examination of the Electrocatalytic Activity of Sr$_2$PdO$_3$ for OER

The electrocatalytic behavior of Sr$_2$PdO$_3$, prepared by the citrate combustion approach for the OER in a 0.1 M HClO$_4$ solution, is appraised by anodic PP. Figure 2 reveals PP curves for the bare GC and GC electrode, modified with the Sr$_2$PdO$_3$ perovskite, in the potential range of 0.9 to 1.5 V vs. Ag/AgCl. It can be detected that the current density, due to the OER, is increased by about 50 times in the presence of the Sr$_2$PdO$_3$ perovskite at a definite potential value of 1.0 V vs. Ag/AgCl. Giordano et al. reported the use of HfN as an efficient catalyst for OER, which gave a current density of about 5 mA cm$^{-2}$ at 1.5 V [11]. Meanwhile, in our case the value of the current density, at 1.5 V, is 8.2 mA cm$^{-2}$. This can be attributed to the catalytic activity of the Sr$_2$PdO$_3$ perovskite for the OER, resultant from the highly stabilized nano-Pd sites within the perovskite matrix [32–35], which utilizes its application as an efficient electrocatalyst for water oxidation.

Figure 2. Potentiodynamic polarization of the unmodified and modified GC electrodes with Sr$_2$PdO$_3$ in a 0.1 M HClO$_4$ solution.
According to the Tafel equation, equation (1) [42]:

$$\eta = a + b \log \frac{I}{I_0}$$

(1)

where $\eta$ is the overpotential (volt), $I$ is the current density ($\text{A cm}^{-2}$), $b$ is Tafel slope (volt), and $a$ is the intercept which is related to the exchange current density, $I_0$, by the equations (2) and (3):

$$a = -b \log I_0$$

(2)

$$b = -\frac{2.3 RT}{\alpha F}$$

(3)

where $F$ is Faraday constant ($96,485 \text{ C mol}^{-1}$), $R$ is the universal gas constant ($8.314 \text{ J.mol}^{-1} \text{ K}^{-1}$), $T$ is the temperature in Kelvin, and $\alpha$ is the transfer coefficient.

The calculated values of the Tafel slope from Figure 2 are 366.3 and 454.1 mV for the bare GC and GC electrode modified with Sr$_2$PdO$_3$, respectively. The value of the Tafel slope usually ranges from 30 to 120 mV and can help to determine whether the slowest step of the reaction is from the first or second electron transfer or the recombination step. In our case, the higher Tafel slope values are observed, indicating additional contributions related to the oxide-surface processes, a potential drop in the anode charge layer, or a blockage of the electrode surface by the bubble accumulations [43–46]. The high Tafel slope values, 200 to 500 mV, were previously reported in literature for the same mentioned reasons [20]. The calculated values of the logarithm of the exchange current density, log $I_0$, which is directly proportional to the rate of the reaction at equilibrium, are $-6.2$ and $-4.4$, ($I_0 = 0.6$ and $39.8 \mu\text{A.cm}^{-2}$) for the bare GC and GC electrode modified with Sr$_2$PdO$_3$, respectively. In other words, the reaction rate at equilibrium is highly increased upon the perovskite modification.

2.3. Determination of the Reaction Order

Figure 3A indicates PP curves for the GC electrode modified with Sr$_2$PdO$_3$ in different concentrations of aqueous HClO$_4$ (0.05 to 0.4 M) at a constant ionic strength by using Na$_2$SO$_4$. This can demonstrate that the rate of the OER is increased with increasing the concentration of the HClO$_4$ solution. The reaction order can be determined from the slope of the logarithm of the current density at a certain potential value, at which a considerable OER is observed, against the pH value of the solution, Figure 3B. The reaction order is 0.81, which is close to unity [20]. This suggests that no further hydroxide ions are adsorbed from the bulk electrolyte before or during the rate-determining step [46–48].

![Graph](image-url)
2.4. Temperature Effect and Activation Energy Determination

The temperature effect on the rate of the OER at Sr₂PdO₅ in a 0.1 M HClO₄ aqueous solution is performed by recording the PP curves at different temperatures (T), from 298 to 328 K, Figure 4A. The reaction rate is favored with the temperature rise. The value of the activation energy (Eₐ) can be determined from the Arrhenius plot, Figure 4B, which equals the slope of log Iₒ vs. 1/T plot, multiplied by −2.3 × R. The calculated value of Eₐ for the OER at Sr₂PdO₅ is 21.6 kJ mol⁻¹, which can be considered a decent value in evaluation with those reported for the transition metal based perovskites, LaBO₃ (B = Fe, Ni, Mn, Co, or Cr) tested in the same electrolyte, Eₐ values from 11.3 to 552.9 kJ mol⁻¹ [20,21], or those of other OER perovskite catalysts in an alkaline medium, Eₐ values from 45.1 to 89.7 kJ mol⁻¹ [49–51]. This reflects the high electrocatalytic activity for Sr₂PdO₅ toward the OER. This can be explained based on the matrix effect of the stable nano-perovskite crystal structure, in which nano-Pd sites are highly distributed and stabilized within the matrix [51–54].
Figure 4. (A) The potentiodynamic polarization of GC/Sr2PdO3 at different temperatures in 0.1 M HClO4 solution, and (B) the corresponding Arrhenius plot.

2.5. Stability

The stability of the proposed Sr2PdO3 catalyst for the OER in a 0.1 M HClO4 solution is examined by performing the reaction at a constant potential of 0.5 V and monitoring the current with the operation time. Figure 5 displays the current-time response of the GC electrode casted with Sr2PdO3 in a 0.1 M HClO4 aqueous solution by being subjected to a constant potential of 0.5 V for 150 min. A sharp current decrease is discerned during the first minutes, which arises from the decrease in the capacitive property. Subsequently, the current due to the OER is almost constant with the decrease in the current at 2.5% after two and a half hours of the catalyst operation. This result reflects the high catalyst stability and excludes any probability of catalyst poisoning. Furthermore, the Sr2PdO3 perovskite presents an enhanced catalytic performance under potentiostatic conditions, as indicated by the increased current value 47.6 µA cm⁻² in assessment with the potentiodynamic experiment, 31.6 µA cm⁻². This can be explicated on the basis that the catalyst undergoes “self-activation” under potentiostatic conditions [53].

Figure 5. The current-time response of the potentiostatic experiment of GC/Sr2PdO3 in 0.1 M HClO4 subjected to a potential of 0.5 V for 150 min.
2.6. Electrochemical Impedance Spectroscopy (EIS)

The mechanism by which the OER occurs at the Sr$_2$PdO$_3$ surface can be analyzed by performing the EIS measurements, according to the classical equation (4); the real part of the impedance, $Z'$, can be expressed as a function of the frequency $\omega$:

$$Z' = R_s + R_p + R_{CT} + \sigma_W \sqrt{\omega}$$  \hspace{1cm} (4)

where $R_s$, $R_p$, and $R_{CT}$ are solution, polarization, and charge-transfer resistances, respectively. $\sigma_W$ is the Warburg impedance.

Figure 6 portrays the EIS spectra, in terms of the (A) Bode and (B) Nyquist plots, of the GC electrode casted with Sr$_2$PdO$_3$ in a 0.1 M HClO$_4$ aqueous solution. The selected overpotential is 0.50 V in the case of the Bode plot and different values for the Nyquist plots: 0.45, 0.50, and 0.55 V. The EIS data reveals the presence of two time constants, as indicated by the two semicircles appearing in the Nyquist plots. The first semicircle, at high frequency regions, is related to the polarization and the double layer capacitance at the perovskite/electrolyte interfaces, $R_p$ and CPE1, while the second semicircle, appearing at intermediate and low frequencies, is related to the charge-transfer and adsorption–desorption processes at the perovskite, $R_{CT}$ and CPE2 [54–57]. The electrical equivalent circuit, illustrated in Figure 6C, is utilized for data fitting and exhibits a good agreement between experimental (circles) and fitted (lines) data. Similar circuits are employed successively for the study of the OER at metals and metal oxides surfaces [58,59]. The electrocatalytic activity of Sr$_2$PdO$_3$ for the OER was explored through the impact of the applied overpotential on the Nyquist plot, Figure 6B. The fitted parameters are presented in Table 1. It can be noted that with increasing the value of the applied overpotential, the value of $R_{CT}$ is decreased, reflecting the high catalytic performance of Sr$_2$PdO$_3$ for the OER. It is worth mention that by increasing the applied overpotential, the diffusion within the perovskite matrix decreases quickly.

![Figure 6](image-url)  \hspace{1cm} Figure 6. The (A) Bode and (B) Nyquist plots GC/Sr$_2$PdO$_3$ in 0.1 M HClO$_4$ at 0.50 V and various overpotentials, respectively. Symbols are experimental and solid lines are modeled data. (C) is the electrical equivalent circuit used for fitting.
Table 1. Fitting parameters obtained by using the electrical equivalent circuit, shown in Figure 6C, for Nyquist plots of GC/Sr2PdO3 in 0.1 M HClO4 solution, at different applied overpotentials.

| Applied Overpotential (V) | Rs (Ω cm²) | CPE1 (µF cm⁻²) | n | Rp (Ω cm²) | CPE2 (µF cm⁻²) | m | Rct (kΩ cm²) | W (mΩ s⁻¹) |
|--------------------------|-------------|----------------|---|------------|----------------|---|------------|-----------|
| 0.45                     | 2.73        | 456.3          | 0.68 | 13.45      | 172.3          | 0.80 | 17.53      | 23.97     |
| 0.50                     | 2.63        | 524.3          | 0.66 | 14.69      | 167.0          | 0.82 | 7.14       | 9.33      |
| 0.55                     | 2.61        | 572.5          | 0.62 | 24.75      | 148.6          | 0.85 | 1.90       | -         |

3. Materials and Method

3.1. Chemicals

Strontium nitrate (99%), palladium (II) chloride (99%), ammonium hydroxide (28–30% NH₃ basis), perchloric acid (ACROS, 70%), nitric acid (70%), citric acid Anhydrous (99.5%), N,N-dimethyl formamide (DMF) (99%), and deionized water. All chemicals were purchased from the Sigma Aldrich Company.

3.2. Synthesis of Sr₂PdO₃ by the Citrate-Nitrate Combustion Method

The preparation through the sol-gel procedure has been reported in detail in a previous work [32,60–63], via mixing Sr(II) and Pd(II) ions in the same molar ratio. Subsequently, citric acid was added to the homogeneous metal ions solution, pH = 2. The solution was kept stirred while heating until complete vaporization, and then it was ignited. The resultant powder was calcined at 750 °C for 3 h to obtain a crystalline perovskite phase.

3.3. Electrochemical Cell and Measurements

The electrochemical measurements were performed in a one-compartment, three-electrode cell in which the working electrode was a glassy carbon (GC) electrode (area = 0.071 cm²), the auxiliary electrode was a platinum coil, and a saturated Ag/AgCl (3.5 M) was used as a reference electrode. The modified electrode, GC/Sr₂PdO₃, was prepared by casting 25 µL of the perovskite suspension in DMF, which was prepared by homogenously mixing 10 mg of perovskite in 1 mL of DMF.

The anodic PP measurements were done in a 0.1 M HClO₄ aqueous solution by first operating an open circuit potential experiment for 10 min until a steady state was reached. This was followed by the conditioning of the working electrode under two-step potentiostatic conditions at 0.4 V for 300 s and at 0.5 V for 600 s, respectively. Finally, the appearance of the PP measure occurred from 0.5 to 1.5 V at a scan rate of 5 mV s⁻¹. All the electrochemical parameters were calculated based on the ohmic drop correction.

The EIS was recorded at different applied overpotentials at a frequency range from 100,000 to 0.1 Hz with an amplitude of 5 mV. All the electrochemical measurements were performed employing a Gamry 1000 potentiostat.

3.4. Sample Characterizations

The X-ray diffractogram was acquired by XRD, Shimadzu, XRD-7000, Japan, at 40 kV and 30 mA, utilizing the CuKα incident beam. The transmission electron microscope (TEM) image is taken by the TEM, JEOL JEM 1400, Japan.

4. Conclusion

Sr₂PdO₃, synthesized through the citrate-combustion methodology, was effectually employed as an electrocatalyst for the OER. The current density was amplified by about 50 times by casting the Sr₂PdO₃ perovskite on the GC substrate and values of Rct, calculated from the Nyquists plots fitting, and was decreased with the upsurge in the applied overpotentials, reflecting a powerful catalytic performance of Sr₂PdO₃ for the OER in 0.1 M HClO₄ solution. This funding is substantiated by the
low values of the calculated activation energy 21.6 kJ mol\(^{-1}\). Sr\(_2\)PdO\(_3\) exhibited a high operation stability with the self-activation property, which promotes its use in water splitting fuel cells.

**Author Contributions:** S.M.A.: Supervision of catalyst preparation, characterizations and electrochemical experiments. Performing data analysis, and writing manuscript. Revision and approval the submitted version of the manuscript. H.M.A.O.: Performing catalyst preparation, characterizations and electrochemical experiments. A.A.E.: Revision and approval the submitted version of the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**

1. Hurst, J.K. In Pursuit of Water Oxidation Catalysts for Solar Fuel Production. *Science* 2010, 328, 315–316, doi:10.1126/science.1187721.
2. Yue, X.; Huang, S.; Cai, J.; Jin, Y.; Shen, P.K. Heteroatoms dual doped porous graphene nanosheets as efficient bifunctional metal-free electrocatalysts for overall water-splitting. *J. Mater. Chem. A* 2017, 5, 7784–7790, doi:10.1039/c7ta01957b.
3. Shu, C.; Kang, S.; Jin, Y.; Yue, X.; Shen, P.K. Bifunctional porous non-precious metal WO\(_2\) hexahedral networks as an electrocatalyst for full water splitting. *J. Mater. Chem. A* 2017, 5, 9655–9660, doi:10.1039/c7ta01527e.
4. Xiao, Z.; Wang, Y.; Huang, Y.C.; Wei, Z.; Dong, C.L.; Ma, J.; Shen, S.; Li, Y.; Wang, S. Filling the oxygen vacancies in CoO\(_x\) with phosphorus: An ultra-efficient electrocatalyst for overall water splitting. *Energy Environ. Sci.* 2017, 10, 2563–2569, doi:10.1039/c7ee01917c.
5. Feng, J.R.; Lv, F.; Zhang, W.; Li, P.; Wang, K.; Yang, Y.; Zhou, J.; Lin, F.; et al. Iridium-Based Multimetalloc Porous Hollow Nanocrystals for Efficient Overall-Water-Splitting Catalysis. *Adv. Mater.* 2017, 29, 1703798, doi:10.1002/adma.201703798.
6. Pi, Y.; Shao, Q.; Wang, P.; Guo, J.; Huang, X. General Formation of Monodisperse IrM (M = Ni, Co, Fe) Bimetallic Nanoclusters as Bifunctional Electrocataysts for Acidic Overall Water Splitting. *Adv. Funct. Mater.* 2017, 27, 1700886, doi:10.1002/adfm.201700886.
7. Fabbri, E.; Habererder, A.; Waltar, K.; Kötz, R.; Schmidt, T.J. Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. *Catal. Sci. Technol.* 2014, 4, 3800–3821, doi:10.1039/C4CY00669K.
8. Herranz, J.; Durst, J.; Fabbri, E.; Pătru, A.; Cheng, X.; Permyakova, A.A.; Schmidt, T.J. Interfacial effects on the catalysis of the hydrogen evolution, oxygen evolution and CO\(_2\)-reduction reactions for (co-)electrolyzer development. *Nano Energy* 2016, 29, 4–28, doi:10.1016/j.nanoen.2016.01.027.
9. Zeng, K.; Zhang, D. Recent progress in alkaline water electrolysis for hydrogen production and applications. *Prog. Energy Combust. Sci.* 2010, 36, 307–326, doi:10.1016/j.pecs.2009.11.002.
10. McCrory, C.C.L.; Jung, S.; Peters, J.C.; Jaramillo, T. Benchmarking Heterogeneous Electrocataysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* 2013, 135, 16977–16987, doi:10.1021/ja407115p.
11. Defilippi, C.; Shinde, D.V.; Dang, Z.; Manna, L.; Hardacre, C.; Greer, A.J.; Agostino, C.D.; Giordano, C. HfN nanoparticles: An Unexplored Catalyst for the Electrocatalytic Oxygen Evolution Reaction. *Angew. Chem. Int. Ed.* 2019, 58, 15464–15470.
12. Suntivich, J.; May, K.J.; Gasteiger, H.A.; Goodenough, J.B.; Shao-Horn, Y. A Perovskite Oxide Optimized for Oxygen Evolution Catalysis from Molecular Orbital Principles. *Science* 2011, 334, 1383–1385, doi:10.1126/science.1212858.
13. Yagi, S.; Yamada, I.; Tsukasaki, H.; Seno, A.; Murakami, M.; Fujii, H.; Chen, H.; Umezawa, N.; Abe, H.; Nishiyama, N.; et al. Covalency-reinforced oxygen evolution reaction catalyst. *Nat. Commun.* 2015, 6, 8249, doi:10.1038/ncomms9249.
14. Grimaud, A.; May, K.J.; Carlton, C.E.; Lee, Y.-L.; Risch, M.; Hong, W.T.; Zhou, J.; Shao-Horn, Y. Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution. *Nat. Commun.* 2013, 4, 2439, doi:10.1038/ncomms3439.
15. Suntivich, J.; Gasteiger, H.A.; Yabuuchi, N.; Nakanishi, H.; Goodenough, J.B.; Shao-Horn, Y. Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries. *Nat. Chem.* 2011, 3, 546–550, doi:10.1038/ncchem.1069.
16. Zhu, Y.; Zhou, W.; Chen, Z.-G.; Chen, Y.; Su, C.; Tadé, M.O.; Shao, Z. SrNb0.8Co0.2Fe0.8O3 Perovskite as a Next-Generation Electrocatalyst for Oxygen Evolution in Alkaline Solution. *Angew. Chem. Int. Ed.* **2015**, *54*, 3897–3901, doi:10.1002/anie.201408998.

17. Takeguchi, T.; Yamanaka, T.; Takakashi, H.; Watanabe, H.; Kuroki, T.; Nakanishi, H.; Orikasa, Y.; Uchimoto, Y.; Takano, H.; Ohguri, N.; et al. Layered Perovskite Oxide: A Reversible Air Electrode for Oxygen Evolution/Reduction in Rechargeable Metal-Air Batteries. *J. Am. Chem. Soc.* **2013**, *135*, 11125–11130, doi:10.1021/ja403476v.

18. Zhu, Y.; Zhou, W.; Chen, Y.; Yu, J.; Xu, X.; Su, C.; Tadé, M.O.; Shao, Z. Boosting Oxygen Reduction Reaction Activity of Palladium by Stabilizing Its Unusual Oxidation States in Perovskite. *Chem. Mater.* **2015**, *27*, 3048–3054, doi:10.1021/acs.chemmater.5b00450.

19. Zhou, W.; Zhao, M.; Liang, F.; Smith, S.C.; Zhu, Z. High activity and durability of novel perovskite electrocatalysts for water oxidation. *Mater. Horiz.* **2015**, *2*, 495–501, doi:10.1039/C5MH00096C.

20. Ali, S.; Al-Rahman, Y.M.A.; Galal, A. Catalytic Activity toward Oxygen Evolution of LaFeO3 Prepared by the Microwave Assisted Citrate Method. *J. Electrochem. Soc.* **2012**, *159*, F600–F605, doi:10.1149/2.063209jes.

21. Ali, S.; Al-Rahman, Y.M.A. Catalytic Activity of LaBO3 for OER in HClO4 Medium: An Approach to the Molecular Orbital Theory. *J. Electrochem. Soc.* **2015**, *163*, H81–H88, doi:10.1149/2.0781602jes.

22. Diaz-Morales, O.; Raaijman, S.; Kortlever, R.; Kooyman, P.J.; Wezendonk, T.; Gascon, J.; Fu, W.T.; Koper, M.T.M. Iridium-based double perovskites for efficient water oxidation in acid media. *Nat. Commun.* **2016**, *7*, 12363, doi:10.1038/ncomms12363.

23. Seitz, L.; Dickens, C.F.; Nishio, K.; Hikita, Y.; Montoya, J.; Doyle, A.; Kirk, C.; Vojvodic, A.; Hwang, H.Y.; Norskov, J.K.; et al. A highly active and stable IrOx/SrIrO3 catalyst for the oxygen evolution reaction. *Science* **2016**, *353*, 1011–1014, doi:10.1126/science.aaf5050.

24. Kumari, S.; Ajayi, B.P.; Kumar, B.; Jasinski, J.B.; Sunkara, M.K.; Spurgeon, J.M. A Low-Noble-Metal W1−IrOx−δ Water Oxidation Electrocatalyst for Acidic Media via Rapid Plasma Synthesis. *Energy Environ. Sci.* **2017**, *10*, 2432–2440.

25. Lu, Y.; Ma, A.; Yu, Y.; Tan, R.; Liu, C.; Zhang, P.; Liu, D.; Gui, J.Z. Engineering Oxygen Vacancies into LaCoO3 Perovskite Electrodes for Efficient Electrocatalytic Oxygen Evolution. *ACS Sustain. Chem. Eng.* **2018**, *7*, 2906–2910, doi:10.1021/acs.suschemeng.8b05717.

26. Goldschmidt, V.M. Die Gesetze der Krystallochemie. *Naturwissenschaften* **1926**, *14*, 477–485, doi:10.1007/bf01507527.

27. Abbes, L.; Noura, H. Perovskite oxides MRuO3 (M = Sr, Ca and Ba): Structural distortion, electronic and magnetic properties with GGA and GGA-modified Becke-Johnson approaches. *Results Phys.* **2015**, *5*, 38–52, doi:10.1016/j.rinp.2014.10.004.

28. Zhou, S.; Miao, X.; Zhao, X.; Ma, C.; Qiu, Y.; Hu, Z.; Zhao, J.; Shi, L.; Zeng, J. Engineering electrocatalytic activity in nanosized perovskite cobaltite through surface spin-state transition. *Nat. Commun.* **2016**, *7*, 11510, doi:10.1038/ncomms11510.

29. Khan, S.; Oldman, R.J.; Corà, F.; Catlow, C.R.A.; French, S.A.; Axon, S.A. A computational modelling study of oxygen vacancies at LaCoO3 perovskite surfaces. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5207–5222, doi:10.1039/b602753a.

30. Kim, G.J.; Lee, S.M.; Hong, S.C.; Kim, S.S. Active oxygen species adsorbed on the catalyst surface and its effect on formaldehyde oxidation over Pt/TiO2 catalysts at room temperature; role of the Pt valence state on this reaction? *RSC Adv.* **2018**, *8*, 3626–3636, doi:10.1039/c7ra11294g.

31. Zheng, Z.; Jia, J.; Zhong, Z. Revisiting the CO oxidation reaction on various Au/TiO2 catalysts: Roles of the surface OH groups and the reaction mechanism. *J. Nanosci. Nanotechnol.* **2014**, *14*, 6885–6893, doi:10.1166/jnn.2014.8943.

32. Galal, A.; Atta, N.F.; Darwish, S.A.; Fatah, A.A.; Ali, S. Electrocatalytic evolution of hydrogen on a novel SrPdO3 perovskite electrode. *J. Power Sources* **2010**, *195*, 3806–3809, doi:10.1016/j.jpowsour.2009.12.091.

33. Atta, N.F.; Ali, S.; El-Ads, E.H.; Galal, A. The Electrochemistry and Determination of Some Neurotransmitters at SrPdO3 Modified Graphite Electrode. *J. Electrochem. Soc.* **2013**, *160*, G3144–G3151, doi:10.1149/2.022307jes.

34. Atta, N.F.; Ali, S.; El-Ads, E.H.; Galal, A. Nano-perovskite carbon paste composite electrode for the simultaneous determination of dopamine, ascorbic acid and uric acid. *Electrochim. Acta* **2014**, *128*, 16–24, doi:10.1016/j.electacta.2013.09.101.
35. Ali, S.M.; Al Lehaibi, H.A. Smart Perovskite Sensors: The Electrocatalytic Activity of SrPdO3 for Hydrazine Oxidation. *J. Electrochem. Soc.* 2018, **165**, B345–B350, doi:10.1149/2.0221809jes.

36. El-Ads, E.H.; Atta, N.F.; Galal, A. The effect of A-site doping in a strontium palladium perovskite and its applications for non-enzymatic glucose sensing. *RSC Adv.* 2016, **6**, 16183–16196, doi:10.1039/C5RA24107C.

37. El-Ads, E.H.; Galal, A.; El-Gohary, A.R. Nano-perovskite decorated carbon nanotubes composite for ultrasensitive determination of a cardio-stimulator drug. *J. Electroanal. Chem.* 2018, **816**, 149–159, doi:10.1016/j.jelechem.2018.03.040.

38. El-Ads, E.H.; Galal, A.; Atta, N.F. Electrochemistry of glucose at gold nanoparticles modified graphite/SrPdO3 electrode—Towards a novel non-enzymatic glucose sensor. *J. Electroanal. Chem.* 2015, **749**, 42–52, doi:10.1016/j.jelechem.2015.04.033.

39. He, J.; Franchini, C. Structural determination and electronic properties of the 4d perovskite SrPdO3. *Phys. Rev. B* 2014, **89**, 45104–45108, doi:10.1103/physrevb.89.045104.

40. Nishihata, Y.; Mizuki, J.; Akao, T.; Tanaka, H.; Uenishi, M.; Kimura, M.; Okamoto, T.; Hamada, N. Self-regeneration of a Pd-perovskite catalyst for automotive emissions control. *Nature* 2002, **418**, 164–167, doi:10.1038/nature00893.

41. Monsi, A.; Foroughi, M.R. Modified Scherrer Equation to Estimate More Accurately Nano-Crystallite Size Using XRD. *World J. Nano Sci. Eng.* 2012, **2**, 154–160, doi:10.4236/wjnse.2012.23020.

42. Fernandes, K.C.; Da Silva, L.M.; Boords, J.F.; De Faria, L.A. Surface, kinetics and electrocatalytic properties of the Ti/(Ti + Ru + Ce)O2-system for the oxygen evolution reaction in alkaline medium. *Electrochim. Acta* 2006, **51**, 2809–2818, doi:10.1016/j.electacta.2005.07.056.

43. Balogun, M.S.; Qiu, W.; Yang, H.; Fan, W.; Huang, Y.; Fang, P.; Li, G.R.; Ji, H.; Tong, Y. A monolithic metal-free electrocatalyst for oxygen evolution reaction and overall water splitting. *Water Environ. Sci.* 2016, **9**, 3411–3416, doi:10.1039/c6we01930g.

44. Reier, T.; Oezaslan, M.; Strasser, P. Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt Catalysts: A Comparative Study of Nanoparticles and Bulk Materials. *ACS Catal.* 2012, **2**, 1765–1772, doi:10.1021/cs2003908.

45. Beck, F.; Krohn, H.; Kaiser, W.; Fryda, M.; Klages, C.; Schäfer, L. Boron doped diamond/titanium composite electrodes for electrochemical gas generation from aqueous electrolytes. *Electrochim. Acta* 1998, **44**, 525–532, doi:10.1016/s0013-4686(98)00115-7.

46. Eigeldinger, J.; Vogt, H. The bubble coverage of gas-evolving electrodes in a flowing electrolyte. *Electrochim. Acta* 2000, **45**, 4449–4456, doi:10.1016/s0013-4686(00)00513-2.

47. Katsuki, N.; Takahashi, E.; Toyoda, M.; Kurosu, T.; Iida, M.; Wakita, S.; Nishiki, Y.; Shimamune, T. Water Electrolysis Using Diamond Thin-Film Electrodes. *J. Electrochem. Soc.* 1998, **145**, 2358, doi:10.1149/1.1838643.

48. Vogt, H.; Balzer, R. The bubble coverage of gas-evolving electrodes in stagnant electrolytes. *Electrochim. Acta* 2005, **50**, 2073–2079, doi:10.1016/j.electacta.2004.09.025.

49. Singh, R.; Singh, N.; Singh, J. Electrocatalytic properties of new active ternary ferrite film anodes for O2 evolution in alkaline medium. *Electrochim. Acta* 2002, **47**, 3873–3879, doi:10.1016/s0013-4686(02)00354-7.

50. Nikolov, I.; Darkaoui, R.; Zhecheva, E.; Stoyanova, R.; Dimitrov, N.; Vitanov, T. Electrocatalytic Activity of Spinel Related Cobaltites MCo3−xO4 (M = Li, Ni, Cu) in the Oxygen Evolution Reaction. *J. Electroanal. Chem.* 1997, **429**, 157–168.

51. Fakhroueian, Z.; Farzaneh, F.; Afrookhteh, N. Oxidative coupling of methane catalyzed by Li, Na and Mg doped BaSrTiO3. *Fuel* 2008, **87**, 2512–2516, doi:10.1016/j.fuel.2008.02.010.

52. Qi, A.; Wang, S.; Fu, G.; Ni, C.; Wu, D. La–Ce–Ni–O monolithic perovskite catalysts potential for gasoline autothermal reforming system. *Appl. Catal. A Gen.* 2005, **281**, 233–246, doi:10.1016/j.apcata.2004.11.038.

53. Tanaka, K.I. Catalysts working by self-activation. *Appl. Catal. A Gen.* 1999, **188**, 37–52, doi:10.1016/s0926-860x(99)00256-2.

54. Harrington, D.A.; Conway, B.E. ac Impedance of Faradaic Reactions Involving Electrosorbed Intermediates-I. Kinetic Theory. *Electrochim. Acta* 1987, **32**, 1703–1712.

55. Galal, A.; Darwish, S.A.; Atta, N.F.; Ali, S.; El Fatah, A.A.A.; Elzatahry, A. Synthesis, structure and catalytic activity of nano-structured Sr–Ru–O type perovskite for hydrogen production. *Appl. Catal. A Gen.* 2010, **378**, 151–159, doi:10.1016/j.apcata.2010.02.015.

56. Atta, N.F.; Galal, A.; Ali, S.; El-Said, D.M. Improved host–guest electrochemical sensing of dopamine in the presence of ascorbic and uric acids in a β-cyclodextrin/Nafion®/polymer nanocomposite. *Anal. Methods* 2014, **6**, 5962–5971, doi:10.1039/c4ay00738g.
57. Atta, N.F.; Galal, A.; Ali, S.; Hassan, S.H. Electrochemistry and detection of dopamine at a poly(3,4-ethylenedioxythiophene) electrode modified with ferrocene and cobaltocene. *Ionics* 2015, 21, 2371–2382, doi:10.1007/s11581-015-1417-z.

58. Conway, B.E.; Liu, T.C. Characterization of electrocatalysis in the oxygen evolution reaction at platinum by evaluation of behavior of surface intermediate states at the oxide film. *Langmuir* 1990, 6, 268–276, doi:10.1021/la00091a044.

59. Wu, G.; Li, N.; Zhou, D.R.; Mitsuo, K.; Xu, B.Q. Anodically electrodeposited Co+Ni mixed oxide electrode: Preparation and electrocatalytic activity for oxygen evolution in alkaline media. *J. Solid State Chem.* 2004, 177, 3682–3692, doi:10.1016/j.jssc.2004.06.027.

60. Galal, A.; Atta, N.F.; Ali, S. Investigation of the catalytic activity of LaBO₃ (B = Ni, Co, Fe or Mn) prepared by the microwave-assisted method for hydrogen evolution in acidic medium. *Electrochim. Acta* 2011, 56, 5722–5730, doi:10.1016/j.electacta.2011.04.045.

61. Galal, A.; Atta, N.F.; Ali, S. Optimization of the synthesis conditions for LaNiO₃ catalyst by microwave assisted citrate method for hydrogen production. *Appl. Catal. A Gen.* 2011, 409, 202–208, doi:10.1016/j.apcata.2011.10.005.

62. Atta, N.F.; Galal, A.; Ali, S.M. The Catalytic Activity of Ruthenates ARuO₃ (A = Ca, Sr or Ba) for the Hydrogen Evolution Reaction in Acidic Medium. *Int. J. Electrochem. Sci.* 2012, 7, 725–746.

63. Atta, N.F.; Galal, A.; Ali, S.M. The Effect of the Lanthanide Ion-Type in LnFeO₃ on the Catalytic Activity for the Hydrogen Evolution in Acidic Medium. *Int. J. Electrochem. Sci.* 2014, 9, 2132–2148.