BILINGUAL PUBLISHING CO.
Pioneer of Global Academics Since 1984

Semiconductor Science and Information Devices
https://ojs.bilpublishing.com/index.php/ssid

ARTICLE

Production of Green Hydrogen by Efficient and Economic Electrolysis of Water with Super-alloy Nanowire Type Electrocatalysts

Linsheng Wang[1,2,3*]

1. Shokubai Wang Institute, Tokyo, Japan
2. National Institute for Materials Science, Tsukuba, Japan
3. The University of Electro-Communications, Tokyo, Japan

ARTICLE INFO

Article history
Received: 30 November 2021
Accepted: 08 December 2021
Published Online: 10 December 2021

Keywords:
Green hydrogen
Zero overpotential
Super-allow nanowires
Electrocatalysts
Electrolysis of water

ABSTRACT

Green hydrogen production from the electrolysis of water has good application prospect due to its renewability. The applied voltage of 1.6-2.2V is required in the traditional actual water electrolysis process although the theoretical decomposition potential of electrolyzing water is 1.23V. The high overpotential in the electrode reaction results in the high energy-consuming for the water electrolysis processes. The overpotentials of the traditional Ru, Ir and Pt based electrocatalysts are respectively 0.3V, 0.4V and 0.5V, furthermore use of the Pt, Ir and Ru precious metal catalysts also result in high cost of the water electrolysis process. For minimizing the overpotentials in water electrolysis, a novel super-alloy nanowire electrocatalysts have been discovered and developed for water splitting in the present paper. It is of significance that the overpotential for the water electrolysis on the super-alloy nanowire electrocatalyst is almost zero. The actual voltage required in the electrolysis process is reduced to 1.3V by using the novel electrocatalyst system with zero overpotential. The utilization of the super-alloy nanowire type electrocatalyst instead of the traditional Pt, Ir and Ru precious metal catalysts is the solution to reduce energy consumption and capital cost in water electrolysis to generate hydrogen and oxygen.

1. Introduction

Green hydrogen production from water splitting in electrolysers, power generation from hydrogen in fuel cells, Li-batteries and Zn-air batteries for energy transformation have recently attracted an increasing attention in past decades [1,2]. Production of green hydrogen by water electrolysis has been a promising strategy to convert the large excess amount of electrical energy from the renewable energy resources [3,4]. When the green hydrogen is used as the fuel in a fuel cells, the energy conversion process not only features high efficiency, but also produces zero emission as it produces only water. Realization of the environment-friendly energy recycle process by developing the water splitting cells for hydrogen production from renewable sources and fuel cells for effective conversion of hydrogen to electricity is highly desirable [5,6]. The efficient and durable electrocatalysts are vital in minimizing the overpotentials for electricity-driven water-splitting in electrolyzers and electrochemical reactions in fuel cells [7,8]. Two half-cell reactions are included in the water electrolysis process and they are oxygen evo-

---

**Corresponding Author:*
Linsheng Wang,
Shokubai Wang Institute, Tokyo, Japan; National Institute for Materials Science, Tsukuba, Japan; The University of Electro-Communications, Tokyo, Japan;
Email: linsheng_wang@yahoo.com

https://doi.org/10.30564/ssid.v3i2.4154

lution reaction (OER) and hydrogen evolution reaction (HER). Water obtained electrons on the anode to release O_2 in OER. OER is rate-determining reaction for water electrolysis process and highly effective and durable catalysts are required to minimize the overpotentials for OER and towards efficient O_2 evolution [9,10]. The three-type of electrolytes including proton exchange membrane (PEM) electrolytes, alkaline electrolytes and high-temperature solid oxide water electrolytes have been studied for water electrolysis so far. Development of stable and non-noble metal OER electrocatalysts with high activity and long term stability in acidic media is still highly challenging [11,12]. Electrocatalysts for oxygen evolution reaction (OER) is the more challenging half-reaction than that for HER in water-splitting reaction. The OER occurs at the anode and involves a four-electron transfer process and a remarkably high overpotential is required by comparison with HER. It has been well known that OER is the major bottleneck in improving the overall efficiency of electrochemical water splitting [13]. Ration design of OER electro-catalysts by understanding of the OER mechanism is contributed to the recent significant progress on the water electrolysis studies. The conventional adsorbate evolution mechanism (AEM) and lattice oxygen-mediated mechanism (LOM) has been widely accepted for OER. The best catalysts with the lowest theoretical overpotential for OER have been found to be IrO_2 and RuO_2 so far [14]. In the acidic electrolyte the noble-metal based electrocatalysts such as Ru and Ir-based catalysts are considered as the state-of-the-art electrocatalyst for OER because it has a larger dissolution resistance compared with other metals [15]. OER electrocatalysts include the noble-metal based electrocatalysts and non-noble metal based electrocatalysts. To reduce the high price and improve the electrocatalyst activity, stability, and enforce the dissolution resistance in acidic media, the strategies to optimize the catalyst composition, structure, and morphology should be considered. Beside Ir and Ru, other noble metals such as Rh, Au, Pt, and Pd-based catalysts have also been developed as bi- or tri-functional electrocatalysts with promising performance for OER, HER, and oxygen reduction reaction (ORR) [16]. The non-noble metal based electrocatalysts such as Ni-Fe based catalysts have received a great deal of interest for OER. Some of non-noble OER catalysts are employed in the industry-scale development including the NiFe-based electrocatalysts. Although RuO_2 and IrO_2 are usually considered as the state-of-the-art electrocatalysts for OER, the high price and serious dissolution of RuO_2 and IrO_2 are the major concerns. Several strategies have been studied to improve the OER electrocatalyst activity and stability and reduce the high cost. The strategies include the heteroatom doping for tuning the composition of IrO_2-based OER electrocatalysts and the Cu-dopant RuO_2 induce the formation of unsaturated Ru sites by Cu dopant to generated O vacancies on the surface. The excellent OER activity is attributed to a combination of the enriched active surface sites, abundant defects, and enhanced surface wettability. In addition, the success in using the cation-exchange process to prepare the active Fe-doped $Co(OH)_2$ nanosheet has demonstrated a new pathway for the fabrication of highly effective OER catalysts [17]. However, many challenging issues are still remained for developing more rational OER electrocatalysts. Shokubai Wang Institute (SWI) has found and developed the Ni-Re super-alloy nano-wires as the unique catalyst materials, which have been applied as the promising catalysts for hydrogen production from methane with water [18]. In the present paper, the electrocatalytic performance of the super-alloy nanowire catalysts for green hydrogen production from electrolysis of water is reported.

2. Experimental

The Ni-Re super-alloy nanowires are available from SWI and the standard Pt catalyst is commercially available. The electrocatalytic performance of the super-alloy nanowires and standard Pt catalyst are tested in an electrochemical station and in a practical Zn-air battery. Electrochemical experimental measurements for rotating disk electrode (RDE) measurements were performed with the electrochemical station by using an Autolab potentiostat/galvanostat in a standard three-electrode configuration with a reversible hydrogen electrode (RHE) as the reference electrode and a Pt foil as the counter electrode at room temperature [19]. A glassy carbon (GC) disk electrode was first polished with alumina past with a particle size of about 0.05μm before electrochemical experimental measurements and it was used as a working electrode. The thin film catalyst layer of the Ni-Re super-alloy nanowires on the GC electrode was prepared by using 12.5 mg catalyst, 18 ml Millipore water and 2 ml Nafion solution (0.5 wt%) ultra-sonicated for 20 min to obtain a well dispersed catalyst ink. The catalyst ink of about 20 μl was then quantitatively put on the GC electrode by using a micropipette and dried in a vacuum to obtain a catalyst thin film. The oxygen evolution reaction (OER) activity was examined by linear sweep voltammetry (LSV) by scanning from 1.0 to 1.8 V vs. RHE in the anodic potential sweep direction and at a scan rate of 10 mV s^{-1} in the electrolyte solution saturated with a flow of pure oxygen by using a MSR rotator from PINE instruments at a rotation speed of 1600 rpm vs. RHE as the reference electrode at a sweep rate of 50 mV s^{-1}.

https://doi.org/10.30564/ssid.v3i2.4154

3. Results and Discussion

Current Hydrogen production is mainly by Steam Methane Reforming (SMR), in which fossil fuels are break apart to produce H_2 and CO_2. This process emits around 9 tons of carbon dioxide per each ton of hydrogen. The current hydrogen production is about 70 million tons, from which more than 98% is from SMR and less than 2% comes from electrolysis and other sources. Hydrogen is a key chemical for ammonia-based fertilizers and could be used in iron ore reduction for the steel industry, biofuel and synthetic hydrocarbons production. These are key industries for our present and future and therefore it is very important to decarbonize them. Hydrogen also has the potential to become an energy carrier to store and transport energy to places and industries that do not have easy access to the electricity grid. Electrolysis of water is a very promising source of hydrogen, but several challenges are still to be addressed. The current cost of electrolyzers is around 900 USD/KW, and one of the major cost being the catalyst materials, which are based on platinum or platinum group metals (PGM). The current service life for electrolyzers is estimated in 10 years. This results in a significant investment cost for electrolysis plants and the need for optimal conditions for amortization. Due to limited efficiency, the current energy consumption in electrolyzers is of around 60 kWh/kgH_2. Therefore, in order to replace all the current SMR hydrogen with electrolytic hydrogen will require energy capacity in the Terawatt range. Figure 1 shows an estimation from IRENA of the target energy cost and capex cost for a viable electrolysis plant that can reach the same price level as SMR hydrogen production. An aggressive reduction in electrolyzer cost is needed as well as a high capacity factor to reach economic viability. The search for alternative cheaper and sustainable catalyst materials is a very important line of research and development. The unique performance of Re-containg catalysts has been found and developed in our previous work for the hydrogen production and utilization. The Re-containing catalysts are used for the following chemical processes [20-32]: i) hydrogen and aromatics production from methane reaction with CO/CO_2; ii) hydrogen production from methane reaction with water; iii) syngas production from methane reaction with CO_2; iv) hydrogen production from water splinting, V) Hydrogenation of aromatics. The above mentioned Re-containg catalysts have been successfully applied in the practical chemical and electrochemical process. They are feasible for scale-up and for the industry application. The catalytic activity of NiRe (Re/Ni=0.05-0.1)/Al_2O_3 is about 10-20 times higher than that of the best Ni/Al_2O_3 catalysts for hydrogen production from methane with water or from methane with CO_2 and for hydrogenation of aromatics; Re/HZSM-5 is the only active catalyst for methane reaction with CO/CO_2 to produce hydrogen and aromatics. The discovery of Ni-Re super-alloy nanowires type catalysts have found the solutions for the some processes of hydrogen energy transformation. The usage of the super-alloy nanowires as the unique catalysts are summarized in Figure 1.

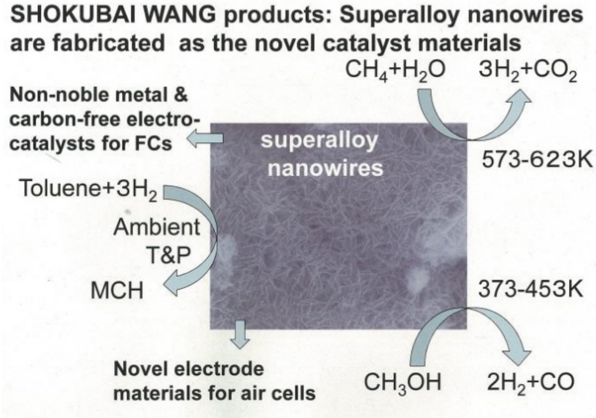

Figure 1. Usage of the Ni-Re super-alloy nanowires as the unique catalysts

The present approaches are to develop the engineered Ni-Re super-alloy nanowires catalyst materials for substitution of the noble-metal catalysts for electrolysis of water. Production of green hydrogen by electrolysis of water with the Ni-Re super-alloy nanowires as the electrocatalyst without containing noble metal elements is the first step for realizing the lower cost for production of hydrogen. Although the theoretical decomposition potential of electrolyzing water is 1.23V, the applied voltage of 1.6-2.2V is required in the traditional actual electrolysis process. The high overpotential in the anode reaction leads to a high energy-consuming and the main energy loss comes from the high overpotential. The overpotentials of Ru, Ir and Pt based electrocatalysts are respectively 0.3V, 0.4V and 0.5V. Furthermore use of the Pt, Ir and Ru precious metal catalysts also result in high cost of the water electrolysis process. On my discovered and developed a new type of non-precious metal alloy nanowire electrocatalyst for water electrolysis to generate hydrogen and oxygen the potential for starting O_2 evolution is about 1.2 V, which is almost same as the theoretic potential for water splitting. This means that the overpotential for water splitting on the Ni-Re super-alloy nanowires catalysts is about zero. It is of significance that the overpotential on my new non-precious metal alloy nanowire electrocatalyst is almost zero. The actual voltage required in the electrolysis process is reduced to 1.3V by using the novel electrocatalyst system with zero overpotential. The utilization of my developed new non-precious metal alloy nanowire type electrocatalyst instead of the traditional Pt, Ir and Ru precious metal catalysts is the solution to reduce energy consumption and capital cost in water electrolysis to generate hydrogen and oxygen. The starting potentials for oxygen evolution reaction (OER) for water splinting on Ni-Re super-alloy nanowires catalyst and on the traditional Pt catalyst are compared in the Figure 2.

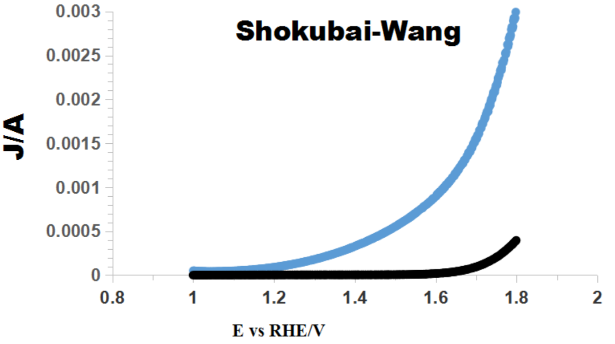

Figure 2. Current J as a function of potential E vs HRE for oxygen evolution reaction (OER) for water splinting on Ni-Re super-alloy nanowires catalyst

We can see from the Figure 2 that the starting potential for oxygen evolution reaction (OER) for water splinting on Ni-Re super-alloy nanowires catalyst is about 1.2V, which is almost same as the theoretical decomposition potential of electrolyzing water (1.23V). This indicates that the overpotential for oxygen evolution reaction (OER) for water splinting on Ni-Re super-alloy nanowires catalyst is about zero, which is much lower than the overpotential for oxygen evolution reaction (OER) for water splinting on the traditional Ru, Ir and Pt nobe metal catalysts. The promising performance of the Ni-Re super-alloy nanowires as the unique electrocatalysts for the oxygen evolution reaction (OEV) in the electrolysis of water to generate the hydrogen and oxygen is contributed to its unique electronic properties and its special nano-wires structure. The oxygen reduction reaction (ORR) in the air-electrode of the Zn-air batteries during the discharge process is the reverse reaction of the oxygen evolution reaction (OER). Therefore, the electro-catalytic performance of the Ni-Re super-alloy nanowires for catalyzing the ORR have been tested as the oxygen catalysts in the air-electrode during the discharge process of Zn-air batteries. The oxygen reduction reaction (ORR) takes place on the air-electrode during the charge process. The ORR on the electrode and the reaction in the Zn-electrode during the discharge process of the Zn-air batteries are briefly expressed as follows,

The reaction in the air-electrode: $1/2O_2 + 2e + H_2O \rightarrow 2OH^- \quad E_0=0.34V$ (1);

The reaction in the Zn-electrode: $Zn - 2e + 2OH^- \rightarrow 1/2Zn(OH)_4^{2-} \quad E_0=1.25V$ (2);

The overall reaction: $1/2O_2 + Zn + H_2O = 1/2Zn(OH)_4^{2-} \quad E_0=1.59V$ (3)

Figure 3 shows the discharge potential (V) with the discharge time at the constant discharge current density of 100 mA/cm^2 in the Zn-air batteries with the Ni-Re super-alloy nanowires as the electrocatalysts in the air-electrode.

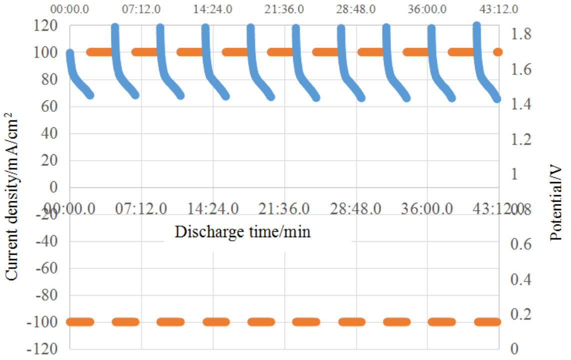

Figure 3. Power density test of Zn-air batteries fabricated by using Ni-Re super-alloy nanowires as oxygen catalyst in air electrode

We can see from the Figure 3 that the maximum discharge potential of about 1.8V and the minimum discharge potential of about 1.4 V attained during the 10 cycles of discharge process at the constant discharge current density of 100mA/cm^2. The obtained peak power density of the Zn-air batteries with the Ni-Re super-alloy nanowires as the oxygen catalyst in the air electrode can be evaluated and it is about 180 mW/cm^2.

The Ni-Re super-alloy nanowires as the electro-catalysts for the oxygen evolution reaction (OER) in the electrolysis of water and for the oxygen reduction reaction (ORR) in the discharge process of the Zn-air batteries have several advantages: i) it exhibits the more promising durability for catalyzing the ORR and OER reactions because of the super-high stability of the super-alloy; ii) it has the excellent conductivity for the electronic transformation and for the heat transformation; iii) it exhibits the super-high catalytic activity for the ORR and OER reactions; iv) the cost is much lower than the noble metal catalysts.

4. Conclusions

The novel super-alloy nanowire electrocatalyst have been discovered and developed for efficient and economical water electrolysis to generate hydrogen and oxygen. It is of significance that the overpotential on the super-alloy nanowire electrocatalyst is almost zero. The actual

https://doi.org/10.30564/ssid.v3i2.4154

voltage required in the electrolysis process is reduced to 1.3V by using the novel electrocatalyst system with zero overpotential. The utilization of the super-alloy nanowire type electrocatalyst instead of the traditional Pt, Ir and Ru precious metal catalysts is the final solution to reduce energy consumption and capital cost in water electrolysis to generate hydrogen and oxygen.

References

[1] S. Wang, A. Lu and CJ Zhong, 2021. Nano Convergence, 8:4.

[2] M.A. Khan, H. Zhao, W. Zou, Z. Chen, W. Cao, J. Fang, J. Xu, L. Zhang, J. Zhang, 2018. Electrochem. Energy Rev. 1(4), 483-530.

[3] A. Li, Y. Sun, T. Yao, H. Han, 2018. Chem. Eur. J. 24(69), 18334-18355.

[4] N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H.M. Chen, 2017. Chem. Soc. Rev. 46(2), 337-365.

[5] F. Yu, L. Yu, I. Mishra, Y. Yu, Z. Ren, H. Zhou, 2018. Mater. Today Phys. 7, 121-138.

[6] X. Zou, Y. Zhang, 2015. Chem. Soc. Rev. 44(15), 5148-5180.

[7] C. Hu, L. Zhang, J. Gong, 2019. Energy Environ. Sci. 12(9), 2620-2645.

[8] Z.P. Wu, X.F. Lu, S.Q. Zang, X.W. Lou, 2020. Adv. Funct. Mater. 30(15), 1910274.

[9] E. Fabbri, T.J. Schmidt, 2018. ACS Catal. 8(10), 9765-9774.

[10] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, 2016. J. Mater. Chem. A 4(45), 17587-17603.

[11] C.J. Zhong, J. Luo, B. Fang, B.N. Wanjala, P.N. Njoki, R. Loukrakpam, J. Yin, 2010. Nanotechnology 21(6), 062001.

[12] R. Loukrakpam, J. Luo, T. He, Y. Chen, Z. Xu, P.N. Njoki, B.N. Wanjala, B. Fang, D. Mott, J. Yin, J. Klar, B. Powell, C.J. Zhong, 2011. J. Phys. Chem. C 115(5), 1682-1694.

[13] W. Wang, Z. Wang, J. Wang, C.J. Zhong, C.J. Liu, 2017. Adv. Sci. 4(4), 1600486.

[14] C.J. Zhong, J. Luo, P.N. Njoki, D. Mott, B. Wanjala, R. Loukrakpam, S. Lim, L. Wang, B. Fang, Z. Xu, 2008. Energy Environ. Sci. 1(4), 454-466.

[15] R. Jiang, S. on Tung, Z. Tang, L. Li, L. Ding, X. Xi, Y. Liu, L. Zhang, J. Zhang, 2018. Energy Storage Mater. 12, 260-276.

[16] C. Zhang, X. Shen, Y. Pan, Z. Peng, 2017. Front. Energy Res. 11(3), 268-285.

[17] S. Sui, X. Wang, X. Zhou, Y. Su, S. Rifat, C.J. Liu, J. Mater, 2017. Chem. A 5(5), 1808-1825.

[18] L. Wang, 2020. Bulletin of Materials Science, 43, 93.

[19] L. Wang, 2019. Bulletin of Materials Science, 42, 85.

[20] L. Wang, Importance & Applications of Nanotechnology, Austin Publishing Group. Vol. 1, Chapter 1, pp. 1-7, 202.

[21] L. Wang, 2021. Advanced Materials Science and Technology. 3:1.

[22] L. Wang Linsheng, 2021. J Mater Sci Nanotechnol, 8(1): 105.

[23] L. Wang, K. Murata, M. Inaba, 2009. Applied Catalysis A: General, 358, 264-268.

[24] L. Wang, K. Murata, Y. Matsumura, M. Inaba, 2006. Energy & Fuels, 20, 1377-1381.

[25] L. Wang, K. Murata, M. Inaba, 2005. Journal of Power Sources, 145, 707-711.

[26] L. Wang, K. Murata, M. Inaba, 2004. Industrial & Engineering Chemistry Research, 43, 3228-3232.

[27] L. Wang, K. Murata, M. Inaba, 2004. Applied Catalysis B: Environmental, 48, 243-248.

[28] L. Wang, K. Murata, M. Inaba, 2004. Applied Catalysis A: General, 257, 43-47.

[29] L. Wang, K. Murata, M. Inaba, 2003. Catalysis Communications, 4, 147-151.

[30] L. Wang, K. Murata, A. Sayari, B. Grandjean, 2001. Chemical Communications, No. 19, 1952-1953.

[31] L. Wang, R. Ohnishi, M. Ichikawa, 2000. Journal of Catalysis, 190, 276-283.

[32] M. Ichikawa, R. Ohnishi, L. Wang, July 30, 2002. United States Patent: 6,426,442.

https://doi.org/10.30564/ssid.v3i2.4154