A Powder Metallurgy Route to Produce Raney-Nickel Electrodes for Alkaline Water Electrolysis

Christian Immanuel Bernäcker, 1 Thomas Rauscher, 2 Tilo Büttner, 1 Bernd Kiebach, 1, 2 and Lars Röntzsch 1, 2

Abstract

Water electrolysis (WE) is the most promising technique to produce hydrogen on industrial scale for a sustainable economy without CO2 emissions (so-called “green hydrogen”). Four different types of WE technologies are known: alkaline water electrolysis (AWE), anion exchange membrane water electrolysis (AEMWE), proton exchange membrane water electrolysis (PEMWE) and solid oxide electrolysis (SOEC). To date, only AWE and PEMWE are available on industrial scale. The large number of manufacturers reflects the significance of WE technology, for example, AREVA, Asahi Kasei, ELB, ErreDue GreenHydrogen, H-Tec Systems, Hydrogenics, Hydrogen-Pro, IHT, ITM Power, McPhy, NEL, PERIC, Siemens, ThyssenKrupp, Wasserelektrolyse Hydrotechnik. The advantage of PEMWE is the operation at high current densities of 1 to 3 A cm⁻² compared to 0.3 to 0.6 A cm⁻² for AWE. Thus, the footprint of PEMWE is usually smaller because the electrolysis stack typically occupies approximately 50% by area of the entire electrolyzer system. However, the investment costs for PEMWE are still significantly higher in comparison to AWE. This is mainly due to the non-automated manufacturing process. In addition, the availability of iridium as anode catalyst material is considered a future bottleneck, because Ir is a secondary metal. AWE will probably overcome these problems in the future, however, some materials challenges mainly related to the stability of the anion exchange membrane have not been solved yet. In comparison to all solid-electrolyte WE technologies, AWE is the most robust and proven technology. Due to the less corrosive alkaline electrolyte, the usage of expensive precious metals can be waived resulting in lower materials and manufacturing costs (CAPEX).

Low-cost green hydrogen is a core component for a sustainable hydrogen economy due the high energy density of hydrogen (lower heating value of 33.33 kWh/kg). Compared to hydrogen production by steam reforming, the costs of hydrogen production by electrolysis are significantly lower since electricity price accounts for most of the production costs of hydrogen by electrolysis. Consequently, automated and high-throughput electrode production processes need to be further developed and established. It is important to note that the electricity price accounts for most of the production costs of hydrogen by electrolysis. In other words, the higher and long-term stable the electrocatalytic activity of the electrodes, the lower the total costs of hydrogen production. In short, the production process as well as the catalytic activity of the electrodes are key parameters for the advanced AWE technology.

Here, we report on a powder metallurgy (PM) route as a promising route to fabricate highly active electrodes. This technology can be applied to flat as well as porous metal electrode template structures. Furthermore, a continuous production process is feasible. Due to the well-proven good electrocatalytic activity of Raney-Ni electrodes for AWE, the production of Raney-Ni electrodes using a PM technology is demonstrated and the activity toward the hydrogen evolution reaction (HER) is discussed.

Experimental

All electrochemical experiments were conducted in a conventional three-electrode configuration in 29.9 wt.% KOH solution at 333 K, considering industrial conditions. For all preparations deionized water (micropure) with conductivity lower than 0.06 μS cm⁻¹ was used. KOH and KCl were obtained from a commercial supplier (VWR) with highest grade. A platinum sheet (8 cm²) was used as counter electrode and a saturated silver/silver chloride electrode (Ag/AgCl sat’d KCl) separated through a Haber-Luggin capillary was utilized as reference electrode. All potentials in this work are referred to this reference electrode (E = 0.197 V vs. NHE at 25°C). The temperature of an electrochemical double walled cell (about 400 ml and made of glass) was controlled by an external thermostat (ΔT = ±2 K) and the solution was purged with N₂ before (at least 30 min) and during the experiments.

A special sample holder (made of polypropylene) was designed in order to study porous electrode materials under realistic conditions, thus, allowing the flow of electrolyte and gas bubbles through the porous electrode sample (see Figure 1).

Unless mentioned otherwise, all current densities are given in relation to the geometric surface area of the electrodes (Ageo = 2 cm²) and are referred to as jgeo. The geometric surface area comprises only the front side of the electrode and neglecting the holes of the used mesh. Consequently, the surface area is underestimated. The real surface area was determined by electrochemical means calculating the double-layer capacitance, Cdl, using cyclic voltammetry (CV). CV was performed in the non-faradaic region at the open circuit potential

© The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0851904jes]
where

\[
\eta_j = \frac{E_j - E_{eq}}{j}
\]

The steady-state polarization curves were recorded galvanostatically in the range from \(j_{geo} = -0.316 \text{ to } -0.1 \times 10^{-3} \text{ A cm}^{-2}\); each step for 20 s in the direction of decreasing current density. The overpotential for the HER, \(\eta\), was determined by

\[
\eta = |E - E_{eq}|
\]

(OCP). Previously, a pretreatment CV was performed to remove all ad- and absorbed H-species from the surface (see Figure 2). After the first CV, no faradaic processes are detected in the region between −0.9 and −0.3 V. The OCP after the pretreatment CV was in this non-faradaic potential window. Referring to McCrory et al., an appropriate potential range of ±0.05 V around the open circuit potential (OCP) and a scan rate from 1 to 0.02 V s\(^{-1}\) in decreasing direction was chosen. The average current densities \(j_{average}\) (see Equation 1) were plotted versus the sweep rate, resulting in a straight line. The slope of the line corresponds to the double-layer capacitance \(C_{dl}\).

\[
j_{average} = \frac{(j_{anodic} - j_{cathodic})}{2}
\]

Figure 1. Schematic drawing of the sample holder.

All electrochemical experiments were carried out without external stirring with a Gamry Reference 3000 potentiostat and were IR-drop corrected (current interrupt method). Prior to the experiments, all samples were carefully washed with deionized water.

Electrochemical experiments (cyclic voltammetry (CV), galvanostatic experiment (GS), Tafel plot) were employed to study the HER activity of the electrodes. A standard test protocol was developed including the following steps:

1. Pretreatment CV: removing ad- and absorbed H-species
2. CV: determining \(C_{dl}\) @OCP before HER
3. GS: determining overpotential (\(\eta_{300}\)) for HER at −300 mA cm\(^{-2}\) after 5 h
4. Tafel plot: potential-current density behavior
5. Pretreatment CV: removing ad- and absorbed H-species
6. CV: determining \(C_{dl}\) @OCP after HER

Electrochemical impedance spectroscopy (EIS) was also used to determine the \(C_{dl}\) @OCP and also to study the HER kinetics (recorded after step 4 at \(\eta = 250, 200, 150, 100, 50, 0 \text{ mV}\)), however the results will be published elsewhere.

The Raney-electrodes were produced in three steps (cf. Figure 3):

Firstly, spraying of an aqueous binder solution followed by the de-leaching of Al powder onto a Ni-mesh; secondly, heat-treatment to the Al-powder—to—Ni-mesh ratio (PMR) (cf. Table I). During heat-treatment, the formation of intermetallic Ni-Al phases takes place (Fig. 3). The corresponding phases are indicated in Figures 4a–4b. The Ni core is completely surrounded by the Ni-Al phases, whereby the leachable phases are predominantly the Ni\(_2\)Al\(_3\) and NiAl\(_3\), where the leaching rate for NiAl\(_3\) is much higher. This effect was confirmed by Alimadadi et al. Subsequently, the Al-Ni electrodes were leached in a potassium hydroxide (1.8 M) and potassium-/sodiumtartrate (1.5 M) aqueous solution at ambient conditions (24 h) and subsequent heated to 353 K (with a fresh leaching solution) until the gas evolution ceased (2–4 h). The samples were washed thoroughly with water. Storage in water is recommended in order to prevent self-ignition of the samples, if exposed to air.

Figure 2. Pretreatment cyclic voltammogram of a Raney-Ni electrode before and after the HER; recorded with 20 mV s\(^{-1}\) at 333 K in a 29.9 wt.-% KOH.

Results and Discussion

Three different Raney-Ni electrodes were prepared by varying the Al-powder—to—Ni-mesh mass ratio (PMR) (cf. Table I). During heat-treatment, the formation of intermetallic Ni-Al phases takes place (Fig. 3). The corresponding phases are indicated in Figures 4a–4b. The Ni core is completely surrounded by the Ni-Al phases, whereby the Al content increases outwardly. However, the thickness is less homogeneous for the RNi4 sample with the lowest PMR value. Alimadadi et al. have studied the phase evolution very precisely with various microscopic techniques and found the same phase formation after 10 to 30 min at 883 K. The precise description of the phase formation mechanism is beyond the scope of this contribution, however, the micrographs in Figures 4a, 4b and 4d coincide with the findings of Alimadadi et al. Subsequently, the Al-Ni electrodes were leached in KOH (aq.) solution in order to produce a high surface area. The leachable phases are predominantly the Ni\(_2\)Al\(_3\) and NiAl\(_3\), whereby the leaching rate for NiAl\(_3\) is much higher. This effect was confirmed

| Sample  | \(j_{0,geo}/\text{mA cm}^{-2}\) | \(-b/\text{mV/dec}\) | \(\eta_{300}/\text{mV}\) | PMR/\text{wt.-%}\) |
|---------|-------------------------------|------------------|------------------|------------------|
| Ni-mesh | 0.427                         | 135              | 393              |                  |
| RNi1    | 9.84                          | 82.3             | 119              | 25.6             |
| RNi2    | 7.92                          | 79.1             | 118              | 17.1             |
| RNi3    | 1.01                          | 85.4             | 125              | 15.8             |
| RNi4    | 2.98                          | 102              | 206              | 10.1             |

Table I. Tafel parameters (exchange current density \(j_{0,geo}\) and the Tafel slope \(b\)) after HER and overpotential values at a current density of −300 mA cm\(^{-2}\) (\(\eta_{300}(\text{HER})\) after 5 h (for RNi2 after 10 h) on the investigated electrodes in a N\(_2\)-purged 29.9 wt.-% KOH solution at 333 K and Al powder-mesh-ratio (PMR) in wt.-%.
within this study. Figure 4c shows the Ni-Al electrode after the leaching procedure. Only the leached Ni$_2$Al$_3$ phase remained atop the Ni core. All phases with a higher Al content were completely dissolved. The thickness of this layer is around 6–8 μm and some Al is still detected in the phase (Fig. 4e).

Only a partial dissolution occurs for Ni$_2$Al$_3$ resulting in a roughened surface structure. Channels oriented perpendicularly to the substrate/surface are observed. It is important to note that no delamination of the porous Ni$_2$Al$_3$ layer was detected, i.e. the Ni core was still completely covered by Ni$_2$Al$_3$. Consequently, porous Ni$_2$Al$_3$ as catalyst is electrically connected to the core of the Ni mesh that acts as a low-resistance electron distributor. These results demonstrate that the process is appropriated to reproduce the formation of a Raney-Ni layer onto a Ni-mesh.

The electrochemical measurements were performed using a special sample holder described above, which reflects realistic conditions in an industrial electrolyzer that uses a classical design (i.e. non-zero gap arrangement). Besides the slow reaction kinetics of the oxygen evolution reaction (OER), the efficiency of the electrolyzer cell is limited by the high overpotential (η) toward HER. Figure 5a outlines the results of the chronopotentiometric measurements. Due to sake of clarity only one representative measurement within the sample batches is given here. The η$_{300}$ value of the bare Ni mesh rises during the first minutes and decreases slightly afterwards up to a value of 393 mV (cf. Table I). Similar behavior has been described in the literature and might be caused by the interplay of hydride formation, reduction of oxide species and the deposition of Fe. A detailed discussion of the effect is beyond the scope of this contribution, however, the in situ deposition of Fe has a major impact causing the slight decrease of η$_{300}$ during the course of the experiment. Although, KOH of highest grade (EMSURE) was used, Fe-impurities in 1 ppm range have to be considered. Using pre-purified KOH solutions might prevent this effect, however, this would reflect unrealistic conditions for a commercial electrolyzer.

The Raney-Ni electrodes exhibit a strongly improved HER activity in comparison to the bare Ni mesh. The η$_{300}$ value ranges between 206 mV and 119 mV, whereas RNi4 exhibits the highest overpotential among all Raney-Ni samples (see Table I). The high HER activity of the Raney-Ni samples is also reflected by the Tafel plots (see Figure 5b). All curves are shifted anodically and exhibit improved Tafel parameters compared to the bare Ni mesh (see Table I, low Tafel-slope b and high exchange current density $j_0$,geo). For the most active Raney-Ni
sample, RNi2, the calculated Tafel slope is 79.1 mV/dec and $j_{0, \text{geo}}$ is 7.92 mA/cm².

In contrast to the Ni electrode, the Raney-Ni samples exhibit a slight increase of $\eta_{300}$ during the first hours, after an activity maximum in the beginning. The loss of activity is more pronounced for the RNi4 electrode. The high degradation rate and higher $\eta_{300}$ value of RNi4 correlates inversely with the lowest PMR value. The active Ni$_2$Al$_3$ layer is more homogeneous distributed around the Ni core at higher PMR values. For the RNi4 samples some cracks are seen and a more pronounced fluctuation of the layer thickness is detected. A high PMR value and in turn a more homogeneous catalyst layer thickness appears to be necessary for a high HER activity as well as a low degradation rate. However, the drop in activity might be associated with the formation of Ni hydride phases as has been proposed by several groups.\textsuperscript{14,26,36,37} The authors suggested that the hydride formation alters the electronic state.\textsuperscript{36} However, there is a controversy about the effect of Ni hydride formation in the literature.\textsuperscript{42} We also would like to mention that the hydride formation is accompanied by the volumetric expansion of the metallic phase (around 6% for Ni).\textsuperscript{38,43–45} This reaction induces internal mechanical stress to the catalytic phase, which in turn can cause the decomposition and/or delamination of the brittle Ni$_2$Al$_3$ catalytic layer as postulated by Soares et al.\textsuperscript{36} This effect appears to have a minor impact for RNi1-3, as can be seen in Figure 6. The SEM images of RN1 were recorded after the HER and depict a roughened catalyst layer over the entire surface. The Raney-Ni layer appears to be strongly connected to the substrate, explaining the low degradation at the end of the GS measurements.

Cyclic voltammetry was used to detect formed Ni hydride species and study the degradation pathway in more detail. The corresponding voltammograms in Figure 7 were recorded before and after the HER. Only for the Raney-Ni samples, the first cycle features two intensive anodic peaks before and after HER: a sharp and intensive peak between $-0.85$ and $-0.6$ V (C2) and a very broad peak between $-0.6$ and 0 V (C3). In some cases a shoulder (C1) at peak C2, shifted to lower overpotentials, can be detected. The peak C2 can be attributed to the oxidation of metallic Ni to Ni$^{2+}$ surface species.\textsuperscript{39,46} C1 and C3 peaks are reflecting the oxidation of a hydrogen species, which are probably associated with the desorption of adsorbed hydrogen species (C1) and to the oxidation of absorbed species (NiH$_x$ to Ni, C3). Due to the fact that the adsorbed species are only existing at the electrode electrolyte interface and the absorbed species are spread into the volume of the bulk, the charge associated with C3 is much larger compared to C1 and C2. In contrast, the second cycle does not feature any anodic or cathodic peaks, illustrating the complete desorption of adsorbed H-species. The bare Ni mesh exhibits only very small anodic peaks (after HER). Possibly, the surface area of the Ni mesh is too low to provide sufficient reaction sites (mainly the grain boundaries)\textsuperscript{47–49} for the diffusion of adsorbed hydrogen into the bulk. Additionally, the hydride phases might not be penetrated too far into the bulk (around 30 $\mu$m for Ni)\textsuperscript{50} and again the low surface area of the mesh makes it not possible to detect electrochemically the hydride species.

Interestingly, for the Raney-Ni samples the ad- and absorbed hydrogen species can be detected before as well as after HER. Before HER, the hydride phases were possibly formed during the leaching process. The intensive evolution of hydrogen during the alkaline dissolution of Al might trigger the metal hydride formation. Interestingly, even after several days of storing the leached electrodes in water, the hydrogen desorption peaks can be seen in the CV.

The peak intensity of all anodic peaks is significantly suppressed after the HER. The overall calculated anodic charge $Q$ (before and after HER) is plotted in Figure 8 versus the materials. The charge $Q$ comprises all anodic reactions (C1, C2 and C3). The charge drop is more pronounced for RNi4 as for RNi2. Due to the fact that the charge $Q$ is associated with the active Ni$_2$Al$_3$ layer, the charge $Q$
is a qualitative indicator for the amount of active catalyst on the Ni mesh. Consequently, the charge drop for RNi4 implies the loss of active catalyst during HER. This coincides with the highest $\eta_{300(\text{HER})}$ value and highest degradation for RNi4 after 5 h. Obviously there is a connection between the activity degradation and the loss of active catalyst.

Due to the thin Ni$_2$Al$_3$ layer and the porous structure of this phase after leaching, the charge $Q$ can also be associated with the electrochemically active surface area. Therefore, the electrochemically active surface area was also determined using CV (see above: test protocol step 2 and 6). The capacitance of the electrode/electrolyte interface, precisely the double-layer capacitance $C_{\text{dl}}$, is proportional to the real electrochemically accessible surface area and can be applied as a qualitative surface parameter. The method is described elsewhere and based on the charging of the double-layer. In order to avoid faradaic reactions, the CVs were recorded at $\pm 0.05$ V around the OCP after discharging the electrode (pretreatment CV). The calculated $C_{\text{dl}}$ values determined before and after the HER are listed in Table II and are also plotted in Figure 9. The results show that the RN11 and RN14 samples possess the highest surface area before the HER (around 41 mF/cm$^2$). For RN12 and RN13 the $C_{\text{dl}}$ is slightly lower at around 29 mF/cm$^2$.

It is very challenging to compare the given data with the literature, since different techniques, conditions, electrodes are used. Mostly, the $C_{\text{dl}}$ is determined employing electrochemical impedance spectroscopy (EIS) at an overpotential $\eta(\text{HER}) > 0$. In this case, the double layer capacitance is superimposed by pseudo-capacitances (e.g. caused by H-adsorption), which makes it difficult to extract the $C_{\text{dl}}$ parameter accurately. From our point of view, the $C_{\text{dl}}$ should be determined at

| Sample   | $C_{\text{dl}}$/mF cm$^{-2}$ Before HER | OCP vs. Ag/AgCl/mV | $C_{\text{dl}}$/mF cm$^{-2}$ After HER | OCP vs. Ag/AgCl/mV |
|----------|------------------------------------------|---------------------|----------------------------------------|---------------------|
| Ni-mesh  | 0.077                                    | 631                 | 0.533                                  | 875                 |
| RN11     | 41.0                                     | 493                 | 30.8                                   | 657                 |
| RN12     | 28.5                                     | 646                 | 37.3                                   | 780                 |
| RN13     | 29.6                                     | 658                 | 29.7                                   | 765                 |
| RN14     | 41.1                                     | 304                 | 5.4                                    | 631                 |
η Raney-Ni electrodes are as follows: tion costs of an electrolyzer, this PM route benefits from a continuous produce highly active Raney-Ni electrodes for alkaline water elec-
cation/delamination of the brittle Ni$_2$Al$_3$ phase from the Ni-substrate tion, due to the loss of surface area. This loss is due to a decompo-
sition/delamination of the brittle Ni$_2$Al$_3$ phase from the Ni-substrate caused by the eruptive detachment of gas bubbles from the electrode surface. Possibly, the low stability of the RNi4 sample might also be linked to the PMR value (see Table 1), which is the lowest for all given RNi samples. It is necessary to study this phenomenon more in detail in the future.

Summary

A powder metallurgy (PM) route is described as a promising route to produce highly active Raney-Ni electrodes for alkaline water electrolysis (AWE). An expanded Ni mesh was used as metallic substrate and the AI-powder-to-Ni-mesh mass ratio (PMR) was varied. The electrocatalytically active Raney-Ni layer was formed in three steps, including the deposition of Al powder, a subsequent heat-treatment and the final leaching of Ni-Al phases. With respect to the production costs of an electrolyzer, this PM route benefits from a continuous process sequence, enabling a high output of electrodes along with a reduced CAPEX for the AWE. The electrochemical results of produced Raney-Ni electrodes are as follows:

- RNi electrodes possess a very high HER-activity with a $\text{n}_{\text{HER}}$ value of 119 mV for RNi1.
- Ad- and absorbed H-species as well as the Ni-oxidation can be detected using cyclic voltammetry. The anodic charge by integrating the CVs correlates with the active surface area.
- The active surface area was also evaluated by determining the double layer capacitance $C_D$ by applying CVs at different scan rate at the OCP ($\pm$ 50 mV). The $C_D$ declines after HER, which might be associated with a loss of active surface area. The main degradation path of the RNi electrodes is associated with the low mechanical stability of the brittle Ni-Al phases. However, the degradation can be significantly reduced (for RN1-3) using a higher PMR value.
- $C_D$ determined after the HER correlates strongly with the HER activity, indicating that the high activity is mainly caused by the very high electrochemically active surface area. The comparably low activity of RNi4 is due to the loss of surface area during HER.

Acknowledgment

This work is part of the ELyntegration project which has received EU funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement no. 671458 and the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract no. 15.0252.

References

1. U. Babic, M. Suermann, F. N. Bucih, L. Guberler, and T. J. Schmidt, J. Electrochem. Soc., 164(4), F387 (2017).
2. L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, and E. Standen, Study on development of water electrolysis in the EU, http://www.fch-ju.eu/sites/default/files/study%20on%20electrolyser%20logos_0.pdf (2014).
3. M. Paidar, V. Fateev, and K. Bouzek, Electrochim. Acta, 209, 737 (2016).
4. S. Maurya, S.-H. Shin, Y. Kim, and S.-H. Moon, RSC Adv., 5(47), 37206 (2015).
5. R. Solmaz and G. Karda˘s, J. Appl. Electrochem., 36(19), 12079 (2011).
6. M. Wolf, J. Caro, A. Feldhoff, P. Steinbach, M. Schultz-Ruhtenberg, and K. Lange, Electrochim. Acta, 252, 430 (2017).
7. C. González-Buch, I. Herraz-Carmona, E. Ortega, J. García-Antón, and V. Pérez-Herranz, J. Appl Electrochem, 46(7), 791 (2016).
8. F. Safizadeh, E. Ghali, and G. Houlachi, Int. J. Hydrogen Energy, 40(1), 256 (2015).
9. K. Lohborg and P. Kohl, Electrochim. Acta, 29(11), 1557 (1984).
10. M. J. de Giz, S. A. S. Machado, L. A. Avaca, and E. R. Gonzalez, AccChemRes., 22(10), 973 (1992).
11. H. Wenk and V. Plizak, Electrochim. Acta, 28(1), 27 (1983).
12. N. Y. Kristjana, J. Gájic-Krstajic, A. Hamdjevac, B. M. Jovic, S. Mora, and V. D. Jovic, Int. J. Hydrogen Energy, 36(11), 6441 (2011).
13. S.-A. Tanaka, N. Hirose, T. Tanaka, and Y. H. Ogata, J. Electrochem. Soc., 147(6), 2240 (2000).
14. L. Chen and A. Lasia, J. Electrochem. Soc., 140(9), 2464 (1993).
15. H. Dong, T. Lei, Y. He, N. Xu, B. Huang, and C. T. Liu, Int. J. Hydrogen Energy, 36(19), 12111 (2011).
16. M. Aghaeihas, M. Mousavi, F. Ben Eltouissi, C. Moreau, R. Wuthrich, and A. Dolatabadi, JSTST, 22(1–2), 220 (2014).
17. D. Chade, L. Berlouis, D. Infield, A. Cruden, P. T. Nielsen, and T. Mathiesen, Int. J. Hydrogen Energy, 38(34), 14380 (2013).
18. L. Barry and A. Lasia, J. Appl. Electrochem., 34, 735 (2004).
19. G. Schiller, R. Henne, P. Mohr, and V. Peinecke, Int. J. Hydrogen Energy, 23(9), 761 (1998).
20. D. Mousse, A. Lasia, and V. Borec, J. Appl. Electrochem., 25(6), 592 (1995).
21. Kostajnic, V. Jovic, and A. L. Antonis, ELECTRODE SUITABLE AS HYDROGEN- EVOLVING CATHODE/EPA/2361324B1 (01.12.2009).
22. M. A. Ramirez and K. L. Willauer, ELECTRODE FOR THE ALKALINE ELECTROLYSIS OF WATER/EPA/3519433 A1 (20.10.2015).
23. S. M. Saha, M. Müller, M. Robinus, and D. Stolten, Int. J. Hydrogen Energy, 43(3), 1209 (2018).
24. W. Kuckshinrichs, T. Ketalet, and J. C. Koja, Front. Energy Res., 5, 151 (2017).
25. T. Liu, R. Reifner, G. Schiller, and A. Ansar, JSTST, 27(1–2), 35 (2018).
26. D. Chade, L. Berlouis, D. Infield, P. T. Nielsen, and T. Mathiesen, J. Electrochem. Soc., 163(3), F308 (2016).
27. S. Marini, P. Salvi, P. Nelli, R. Pesenti, M. Villa, M. Berrettoni, G. Zangari, and Y. Kiros, Electrochim. Acta, 82, 584 (2012).
28. K. Zeng and D. Zhang, Prog. Energy Combust. Sci., 36, 307 (2010).
29. J. Bajel, J. Divisek, H. Schmitz, and J. Mergel, J. Appl. Electrochem., 22(8), 711 (1992).
30. A. J. Bard and L. R. Faulkner, Electrochemical methods: Fundamentals and applications, New York, Wiley (2001).
31. S. Trasatti and O. A. Petriu, J. Electroanal. Chem., 327(1–2), 353 (1992).
32. R. K. Shervedani and A. Lasia, J. Appl. Electrochem., 29(8), 799 (1999).
33. C. C. L. McCrory, S. Jung, J. C. Peters, and T. F. Jaramillo, J. Am. Chem. Soc., 135(43), 16977 (2013).
34. H. Alimadadi, C. Kjartansdottir, A. Burrows, T. Kasama, and P. Møller, JSTST, 160(9), F387 (2017).
35. C. Kjartansdottir, L. P. Nielsen, and P. Møller, Int. J. Hydrogen Energy, 38(20), 8221 (2013).
36. D. M. Soares, O. Teschke, and I. Torrià, J. Electrochem. Soc., 139(1), 98 (1992).
37. H. E. G. Rommal and P. J. Morgan, J. Electrochem. Soc., 135(2), 343 (1988).
38. I. Paseka, Electrochim. Acta, 50(13), 4537 (2005).
39. D. S. Hall, C. Bock, and B. R. MacDougall, J. Electrochem. Soc., 160(3), F235 (2013).
40. A. E. Maier, D. W. Kirk, and S. J. Thorpe, J. Electroanal. Chem., 52(11), 3505 (2007).
41. I. Fliis-Kabulska, J. Flis, Y. Sun, and T. Zakroczymska, Electrochim. Acta, 167, 61 (2015).
42. S. Marini, P. Salvi, P. Nelli, R. Pesenti, M. Villa, and Y. Kiros, Int. J. Hydrogen Energy, 38(26), 11484 (2013).
43. J. M. Joubert, M. Latroche, R. Černý, A. Percheron-Guégan, and K. Yvon, 
   *J. Alloys Compd.*, 330–332, 208 (2002).
44. C. Pohlmann, K. Herbrig, L. Gondek, N. Kardjilov, A. Hilger, H. Figiel, J. Banhart, 
   B. Kieback, I. Manke, and L. Röntzsch, *J. Power Sources*, 277, 360 (2015).
45. C.-K. Lin and Y.-C. Chen, *Renewable Energy*, 48, 404 (2012).
46. R. S. Schreiber Guzmán, J. R. Vilche, and A. J. Arvía, *J. Appl. Electrochem.*, 8(1), 
   67 (1978).
47. G. Majer, U. Eberle, F. Kimmerle, E. Stanik, and S. Orimo, *Physica B: Condensed 
   Matter*, 328(1–2), 81 (2003).
48. A. Zaluska, L. Zaluski, and J. O. Ström-Olsen, *Appl Phys A*, 72(2), 157 (2001).
49. L. Zaluski, A. Zaluska, and J. O. Ström-Olsen, *J. Alloys Compd.*, 253–254, 70 
   (1997).
50. B. Baranowski and S. M. Filipiak, *Journal of Alloys and Compounds*, 404–406, 2 
   (2005).
51. E. Gileadi, *Physical electrochemistry: Fundamentals, techniques and applications: 
   580*, Weinheim, Wiley-VCH-Verl. (2011).
52. T. Rauscher, C. I. Müller, A. Gabler, T. Gimpel, M. Köhring, B. Kieback, W. Schade, 
   and L. Röntzsch, *Electrochimica Acta*, (247), 1130 (2017).
53. S. Anantharaj, S. R. Edie, K. Karthick, S. Sam Sankar, K. Sangeetha, P. E. Karthik, 
   and S. Kundu, *Energy Environ. Sci.*, 11, 744 (2018).
54. L. Wu, Y. He, T. Lei, B. Nan, N. Xu, J. Zou, B. Huang, and C. T. Liu, *Mater. Chem. 
   Phys.*, 141(1), 553 (2013).
55. L. Wu, Y. He, T. Lei, B. Nan, N. Xu, J. Zou, B. Huang, and C. T. Liu, *Energy*, 63, 
   216 (2013).