

# Decoupled Water Splitting for Green Hydrogen Production: Reshaping Water Electrolysis

By Avner ROTHSCCHILD

Department of Materials Science and Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Hen DOTAN

H2Pro, 2 Ha-Tokhen street, Caesarea Business and Industrial Park, Israel

And Gideon GRADER

Department of Chemical Engineering, Technion – Israel Institute of Technology, Haifa, Israel

Green hydrogen production at scale is essential to fight global warming and climate change. The present water electrolysis technologies present significant barriers to meet this challenge, due to high system and operational costs that emerge from the need to divide each cell into gas-tight cathodic and anodic compartments to avoid mixing hydrogen with oxygen, and from intrinsic energy losses in the complex oxygen evolution reaction. Recent efforts to overcome these barriers include transformative approaches to decouple the hydrogen and oxygen evolution reactions using soluble redox couples or solid redox electrodes that mediate the ion exchange between the primary electrodes such that hydrogen and oxygen are generated at different times and/or different cells. This leads the way to membraneless electrolyzer architectures that can enhance safety, reduce system costs, and provide operational advantages such as high-pressure hydrogen production. In particular, E-TAC water splitting offers these advantages as well as ultrahigh efficiency and compact design of rolled electrode assemblies, opening new frontiers for advanced water electrolysis.

## Introduction

Green hydrogen produced from water using electricity from renewable energy sources such as solar and wind is essential to reduce CO<sub>2</sub> emissions, especially in hard-to-abate industrial sectors such as steel, cement and ammonia production. Such hydrogen is a critical component in the energy transition to fight climate change. Energy economy analysts estimate it will contribute between 12 and 22% of the global energy demand in 2050<sup>(1)</sup>. The present technologies for green hydrogen production are alkaline water electrolysis (AWE) and polymer electrolyte membrane water electrolysis (PEMWE). In addition, high-temperature solid oxide water electrolysis (SOWE) emerges as a new technology that promises ultrahigh efficiency but struggles to achieve long-term stability, especially under thermal cycling, as well as low cost<sup>(2)</sup>.

One thing in common to all three technologies is the coupling between the hydrogen and oxygen evolution reactions (HER and OER, respectively), where both

reactions occur concurrently in the same electrolytic cell<sup>(3)</sup>. Therefore, a Nafion membrane (in PEMWE)<sup>(4)</sup> or Zirfon diaphragm (in AWE)<sup>(5)</sup> divides the cell into two gas-tight compartments to avoid hazardous H<sub>2</sub>/O<sub>2</sub> mixing, as illustrated schematically in Figure 1 from the page 145. This membrane electrolysis architecture complicates the electrolyzer's construction by adding gaskets and compression sealing over large areas to prevent H<sub>2</sub>/O<sub>2</sub> crossover. This adds substantial costs and limits operation at high pressures and low-purity water.

Energy conversion efficiency is another grand challenge for this energy-intensive technology, where alkaline electrolyzers consume between 50 and 78 kWh per kg

<sup>(1)</sup> SÖNNICHSEN N. (2022), "Global hydrogen demand estimates as share of total energy 2050", by outlook scenario, Statista.

<sup>(2)</sup> International Renewable Energy Agency – IRENA (2020), "Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal", report.

<sup>(3)</sup> CHATENET M., POLLET B. G., DEKEL D. R., DIONIGI F., DESEURE J., MILLET P., BRAATZ R. D., BAZANT M. Z., EIKERLING M., STAFFELL I., BALCOMBE P., SHAO-HORN Y. & SCHÄFER H. (2022), "Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments", *Chem. Soc. Rev.* 51, pp. 4583-4762.

<sup>(4)</sup> AYERS K., DANILOVIC N., HARRISON K. & XU H. (2021), "PEM electrolysis, a forerunner for clean hydrogen", *Electrochem. Soc. Interface* 30, p. 67.

<sup>(5)</sup> BRAUNS J., SCHÖNEBECK J., KRAGLUND M. R., AILI D., HNÁT J., ŽITKA J., MUES W., JENSEN J. O., BOUZEK K. & TUREK T. (2021), "Evaluation of diaphragms and membranes as separators for alkaline water electrolysis", *J. Electrochem. Soc.* 168, 014510.

of hydrogen produced<sup>(2)</sup>, which translates to a system efficiency of 50 to 79% based on the higher heating value (HHV) of hydrogen (39.4 kWh/kg<sub>H<sub>2</sub></sub>). PEM electrolyzers consume a bit more energy (50-83 kWh/kg<sub>H<sub>2</sub></sub>) than their alkaline counterparts, whereas high-temperature solid oxide electrolyzers present higher efficiency (45-55 kWh/kg<sub>H<sub>2</sub></sub>) but also higher capital costs and shorter lifetime compared to their low-temperature alkaline and PEM counterparts<sup>(2)</sup>. Thus, 25 to 50% of the electrical energy is lost in vain in traditional water electrolysis. The lion's share of this loss, in state-of-the-art electrolyzers, arises from the OER due to a thermodynamic barrier that emerges from the four proton-coupled electron transfer steps necessary to produce an O<sub>2</sub> molecule, which leads to a high overpotential of 0.3-0.4 V at the onset of oxygen evolution<sup>(6)</sup>.

These drawbacks burden the cost of green hydrogen production, and the dependence on critical raw materials of alkaline, PEM and solid oxide electrolyzers limits their scale-up potential<sup>(7)</sup>. Overcoming these barriers is necessary to reach green hydrogen production<sup>(2)</sup> at terawatt scale in order to support the Net Zero transition. Incremental improvements of present technologies support reaching short-term goals, but frontier research and innovation that aim at developing breakthrough materials and processes for next generation technologies are necessary to achieve long-term goals. Thus, advanced materials and novel cell designs for next generation water electrolysis technologies is a topmost research priority towards Net Zero<sup>(8)</sup>. In particular, membraneless cell architectures present a promising potential for cost reduction, compact and more efficient systems as well as operational advantages such as high-pressure hydrogen production<sup>(9)</sup>. Specifically, decoupled water electrolysis (DWE) where the HER and OER are decoupled in time and/or place presents an emerging concept that attracts growing interest in the past decade<sup>(10) and (11)</sup>. This decoupling leads the way to safe operation without membranes in some DWE

schemes, as in the case of E-TAC water electrolysis<sup>(12)</sup>, and provides new opportunities to reshape water electrolysis and potentially overcome the fundamental barriers of this two centuries-old technology<sup>(13)</sup>.

## Decoupled water electrolysis (DWE)

DWE was first reported by Symes and Cronin in 2013, based on adding to the electrolyte a soluble redox couple (SRC) that functions as an electron-coupled-proton buffer and mediates the proton exchange between the anodic and cathodic reactions (OER and HER, respectively), as illustrated schematically in Figure 1b from the page 145<sup>(14)</sup>. Despite generating oxygen and hydrogen in different stages, a membrane was still required to prevent redox shuttling between the anode and cathode, and the efficiency was lower (52%<sub>HHV</sub>) than in conventional water electrolysis. Low efficiency is an inherent disadvantage of this method since the oxidation and reduction overpotentials of the SRC add up to those of the OER and HER, thus necessitating a larger voltage than in conventional water electrolysis<sup>(13)</sup>. Subsequent studies pursuing this approach introduced different SRCs and operation schemes, but the efficiency remained low and a membrane was still necessary<sup>(10,11 and 13)</sup>. Another disadvantage common to all the systems reported employing this approach is the use of platinum group metal (PGM) catalysts due to operation in acidic electrolytes where non-noble metals and their oxides are unstable.

A different DWE approach was reported by Chen *et al.*<sup>(15)</sup> and by Landman *et al.*<sup>(16)</sup>, using solid redox electrodes (SRE) instead of SRC, and operating in alkaline instead of acidic electrolytes. Using nickel (oxy) hydroxide electrodes from rechargeable alkaline batteries (e.g., the cathodes in NiCd batteries) as auxiliary electrodes that mediate the OH<sup>-</sup> exchange between the cathode and anode of alkaline water electrolysis, the electrolytic cell is divided into two separated cells that generate hydrogen and oxygen remotely from each other, as illustrated schematically in Figure 1c from the page 145. This enables operation without membranes/diaphragms, paving the way for membraneless

<sup>(6)</sup> MAN I. C., SU H.-Y., CALLE-VALLEJO F., HANSEN H. A., MARTÍNEZ J. I., INOGLU N. G., KITCHIN J., JARAMILLO T. F., NØRSKOV J. K. & ROSSMEISL J. (2011), "Universality in oxygen evolution electrocatalysis on oxide surfaces", *ChemCatChem* 3, pp. 1159-1165.

<sup>(7)</sup> KIEME S. I. S., MOLINKA T., LEHNER F., FULL J., SAUER A. & MIEHE R. (2021), "Critical materials for water electrolyzers at the example of the energy transition in Germany", *Int. J. Energy Res.* 45, pp. 9914-9935.

<sup>(8)</sup> Hydrogen Europe Research (2022), position paper titled "For a long perspective impact of European Research and Industrial Sectors".

<sup>(9)</sup> ESPOSITO D. V. (2017), "Membraneless electrolyzers for low-cost hydrogen production in a renewable energy future", *Joule* 1, pp. 651-658.

<sup>(10)</sup> MCHUGH P. J., STERGIOU A. D. & SYMES M. D. (2020), "Decoupled electrochemical water splitting: From fundamentals to applications", *Adv. Energy Mater* 10, 2002453.

<sup>(11)</sup> IFKOVITS Z. P., EVANS J. M., MEIER M. C., PAPADANTONAKIS K. M. & LEWIS N. S. (2021), "Decoupled electrochemical water-splitting systems: a review and perspective", *Energy Environ. Sci.* 14, pp. 4740-4759.

<sup>(12)</sup> DOTAN H., LANDMAN A., SHEEHAN S. W., MALVIYA K. D., SHTER G. E., GRAVE D. A., ARZI Z., YEHUDAI N., HALABI M., GAL N., HADARI N., COHEN C., ROTHSCHILD A. & GRADER G. S. (2019), "Decoupled hydrogen and oxygen evolution by a two-step electrochemical – Chemical cycle for efficient overall water splitting", *Nature Energy* 4, pp. 786-795.

<sup>(13)</sup> LANDMAN A., ROTHSCHILD A. & GRADER G. (2021), "New electrolyzer principles: Decoupled water splitting", in *Hydrogen Production by Water Electrolysis*, edited by SMOLINKA T. & GÄRCHE J., Elsevier.

<sup>(14)</sup> SYMES M. D. & CRONIN L. (2013), "Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer", *Nature Chemistry* 5, pp. 403-409.

<sup>(15)</sup> CHEN L., DONG X., WANG W. & XIA Y. (2016), "Separating hydrogen and oxygen evolution in alkaline water electrolysis using nickel hydroxide", *Nature Communication* 7, 11741.

<sup>(16)</sup> LANDMAN A., DOTAN H., SHTER G. E., WULLENKORD M., HOUAIJIA A., MALJUSCH A., GRADER G. S. & ROTHSCHILD A. (2017), "Photoelectrochemical water splitting in separate oxygen and hydrogen cells", *Nature Materials* 16, pp. 646-651.

decoupled water electrolysis (MLDWE). The disadvantage of replacing the mobile SRC that flows with the electrolyte from one cell to another by stationary SRE is that this requires batch operation to regenerate the auxiliary electrodes when they reach their maximal capacity, whereas SRCs support continuous operation as in traditional electrolyzers<sup>(10, 11 and 13)</sup> Although the reported systems are less efficient than AWE<sup>(15 and 16)</sup> for the same reason as described above for the case of SRC, they might serve unique purposes such as photoelectrochemical water splitting with centralized hydrogen production<sup>(16 and 17)</sup>.

Another DWE approach was reported by Rausch *et al.*<sup>(18)</sup>, introducing an electrochemical – Chemical cycle (ECC) whereby an SRC (silicotungstic acid) was

reduced electrochemically at the cathode while oxygen evolved at the anode of an electrolytic cell, and then transferred into another cell where it was oxidized chemically and released hydrogen upon contact with a platinum catalyst (without applying electricity). The electrolytic efficiency was 62%<sub>HHV</sub>, lower than in conventional water electrolysis, and a membrane was used to prevent redox shuttling in the electrolytic cell. Other ECCs with different SRCs were reported, in acidic electrolytes, using PGM catalysts and achieving lower efficiency than in conventional water electrolysis<sup>(10,11 and 13)</sup>.

## E-TAC water splitting

An exciting breakthrough in DWE was reported by Dotan *et al.* in 2019, introducing an electrochemical – Thermally-activated chemical (E-TAC) cycle that divides the OER into two sub-reactions and enables operation at near thermoneutral conditions<sup>(12)</sup>. In the first stage (E), a cobalt-doped nickel hydroxide anode was charged to nickel oxyhydroxide while hydrogen evolved at the cathode. This stage was done in a cold (~25°C) alkaline electrolyte (lye), and it was stopped before

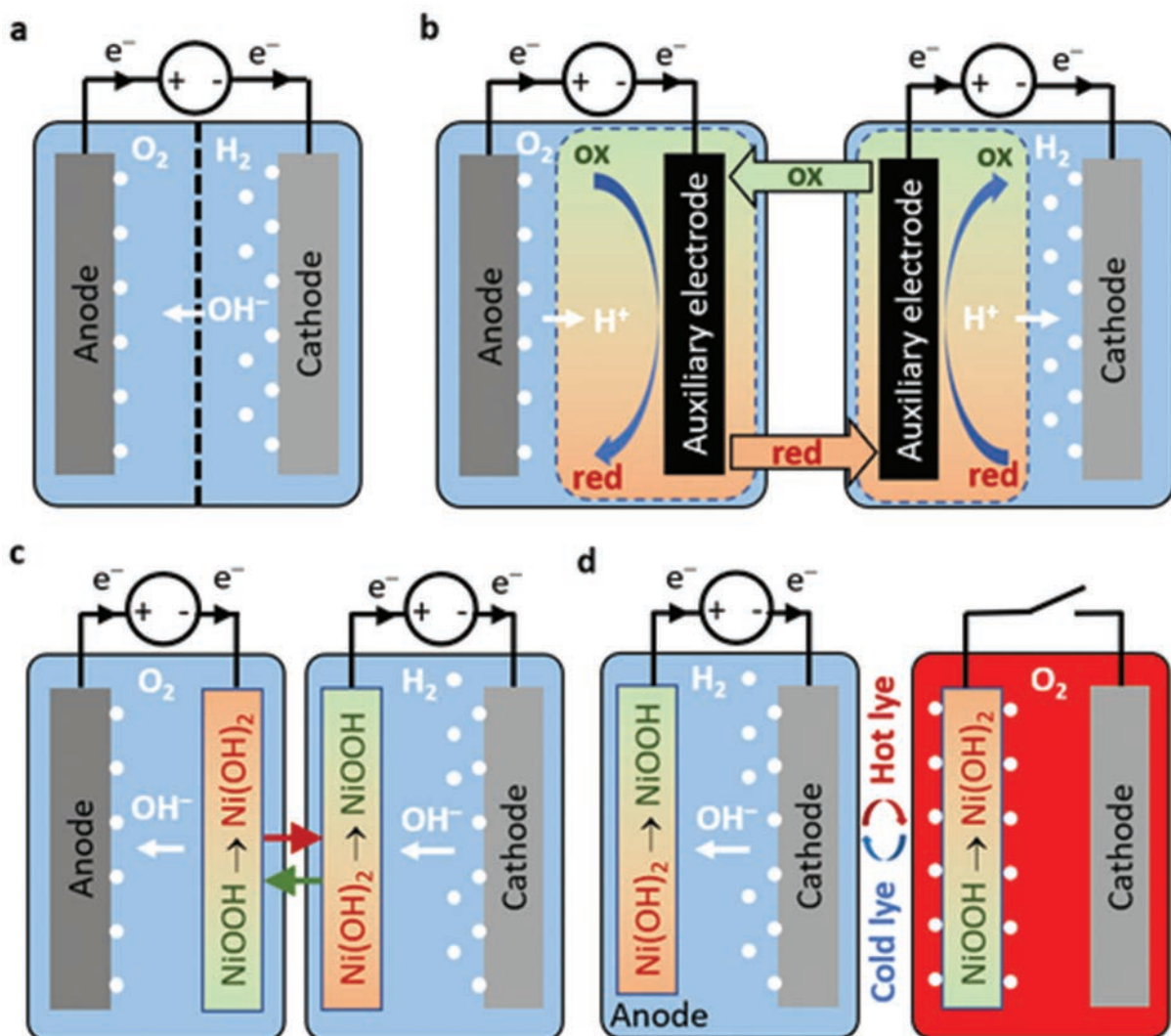


Figure 1: Schematic illustrations of the basic operation at cell level in: a) alkaline water electrolysis; b) decoupled water electrolysis with a soluble redox couple; c) decoupled water electrolysis with solid redox electrodes; and d) electrochemical – thermally-activated chemical (E-TAC) decoupled water electrolysis.

oxygen started to evolve at the charged anode, such that only hydrogen was produced in this stage. Then, in the second stage (TAC), the cold lye was replaced by a hot (95°C) lye that induced a fast spontaneous reaction between the charged anode and water, regenerating the anode back to its initial state while producing oxygen,  $4\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 4\text{Ni(OH)}_2 + \text{O}_2$ , as illustrated in Figure 1d from the previous page. The heat generated in this exothermic reaction heats the system in the TAC stage, whereas the heat absorbed in the endothermic electrochemical reaction cools the system in the E stage. Therefore, in an ideal system, no external energy source is needed to supply the required heat for the thermal swings of the E-TAC cycle.

The E-TAC process presents important advantages such as ultrahigh efficiency (98.7%<sub>HHV</sub> at cell level) and membraneless operation<sup>(12)</sup>, identifying it as a promising competitive alternative to conventional water electrolysis<sup>(19)and(20)</sup>. Its membraneless architecture leads the way to simple cell designs, such as rolled electrodes that can be piled up to form a compact stack, as shown in Figure 2. This demonstrates a unique advantage

over traditional membrane electrolysis which is limited to a parallel plate architecture where compression sealing prevents H<sub>2</sub>/O<sub>2</sub> crossover between the cathodic and anodic compartments. Operating in alkaline electrolyte where nickel-based materials can replace the PGM catalysts used in acidic electrolytes (as in PEMWE) means that all the cell components can be made of Earth-abundant elements. The E-TAC process also presents technological challenges that emerge from batch operation with thermal swings between the E and TAC stages, as well as from capacity and rate limitations for charge storage at the nickel (oxy)hydroxide anodes. These challenges are addressed by H<sub>2</sub>Pro, an Israeli startup company that develops ultra-efficient high-pressure (50 bar) water electrolysis systems for green hydrogen production at scale, based on the innovative E-TAC process<sup>(21)</sup>. H<sub>2</sub>Pro started operating in 2019, and has since raised more than USD 100 million. Amongst the high profile investors are Breakthrough Energy Ventures, Horizons Ventures and Temasek Holdings as well as Yara and Arcelor Mittal. The company has grown to nearly 100 employees, mostly in R&D. The company concentrates on the development of its special rolled electrodes

<sup>(19)</sup> SYMES M. D. (2019), "Decoupled electrolysis – Just add hot water", *Nature Energy* 4, pp. 730-731.

<sup>(20)</sup> CENTI G. (2022), "Across the board: Gabriele Centi on decoupling electrocatalytic reactions to electrify chemical production", *ChemSusChem* 15, e202200007.

<sup>(21)</sup> ROTHSCHILD A., LANDMAN A., DOTAN H., SHTER G. & GRADER G. (2020), *Methods and system for hydrogen production by water electrolysis*, United States Patent No. 2020/0040467 A1.

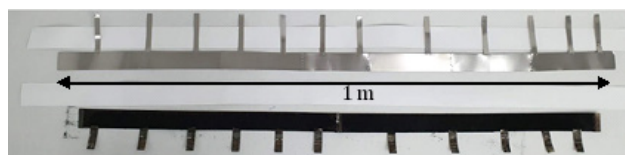


Figure 2a: E-TAC electrodes – Photo@H<sub>2</sub>Pro.



Figure 2b: Rolled electrodes – Photo@H<sub>2</sub>Pro.



Figure 2c: A stack of rolled electrodes – Photo@H<sub>2</sub>Pro.



Figure 2d: two E-TAC reactors containing such stacks – Photo@H<sub>2</sub>Pro.

and systems as shown below. It plans to complete its first factory in 2023/24 and start sales in 2024/25. H<sub>2</sub>Pro is stating that the unique advantages of the E-TAC technology will allow it to sell multi megawatts systems for as low as 200 \$/kW, before the end of the decade. H<sub>2</sub>Pro economic analysis predicts that the low Capex of the system and their high efficiency will allow to achieve the Energy Earth-shot initiative goal of 1\$ for 1 kg of green hydrogen before the end of the decade<sup>(22)</sup>.

## Summary and conclusions

In conclusion, it is clear that there is a global consensus that large scale production of green hydrogen is essential for mankind to win the battle against global warming and climate change. This battle will be fought on many

levels and fronts including green hydrogen production, storage, transportation, compression, purification and more. Clearly the production step is a key enabling step in the long and complex chain required to win this battle. Decoupled water electrolysis wherein the hydrogen and oxygen evolution reactions are decoupled in time and/or place present new opportunities to enhance safety, reduce system costs, and provide operational advantages such as high-pressure hydrogen production, with respect to traditional electrolyzes. In particular, E-TAC water splitting presents all these advantages and more, offering ultrahigh efficiency and compact design of rolled electrodes. These unique advantages readily lend themselves to automation and robotic production of large area rolled electrodes, much like the fabrication of batteries. This endows the E-TAC technology with a significant advantage in large scale production of electrodes and systems for green hydrogen production at terawatt scale.

<sup>(22)</sup> <https://www.energy.gov/eere/fuelcells/hydrogen-shot#:~:text=The%20first%20Energy%20Earthshot%2C%20launched,%221%201%201%22>