On the use of chlor-alkali technology to power environmental electrochemical treatment technologies

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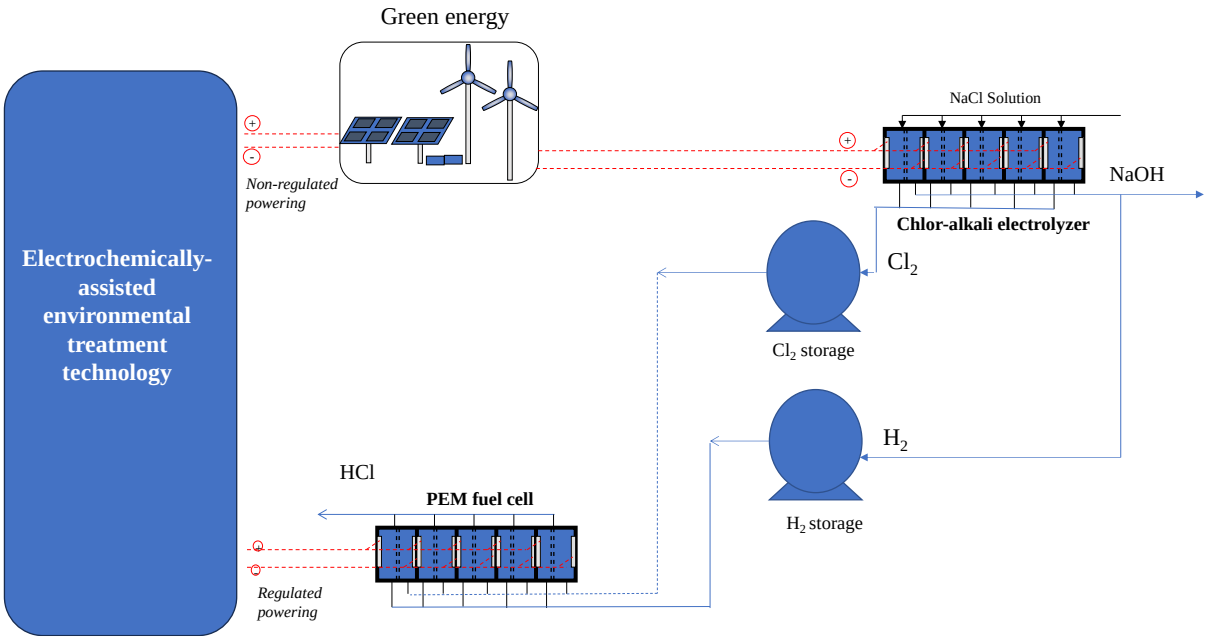
Abstract

This review tries to differ from the existing reviews on the potential of chlor-alkali technology in regulating energy for environmental remediation through hydrogen-based storage. Currently, green energies are at a very high technology readiness level, but fitting demand and production of energy is not a solved issue. Direct application in environmental treatments is inefficient, particularly in electrokinetic because of reversibility. Hydrogen-based energy storage shows promise, despite water management challenges in electrolyzers, especially in drought-prone regions like the Mediterranean countries. This review suggests adapting chlor-alkali technology from industrial to environmental contexts as a less water-demanding alternative. It also shows the adaptability of electrolyzers, contrasting it with the challenges faced by fuel cells due to chlorine's corrosive effects. It concludes that the sustainable solution proposed involves synergistic chlor-alkali electrolysis and PEM fuel cells using oxygen instead of chlorine, benefiting the industry affected by electricity price increases. Byproducts like chlorine and caustic soda can be repurposed for environmental or commercial purposes.

Keywords

Chlor-alkali; reversible electrochemical cells; gas-liquid cells; hydrogen storage; powering; environmental electrochemistry.

Graphical abstract



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1. Necessity of energy storage for the application of electrochemical technologies in environmental remediation

There is a growing concern about the development of more and more sustainable treatment technologies that can help to mitigate the impact of the human activities on the environment. In addition, there is special interest in minimizing the effect on climate change and water reservoir preservation of already existing technologies[1]. Likewise, within the new paradigm of circular economy, there is a need to develop technologies that minimize the use of natural resources, considering not only reagents as those resources whose use has to be optimized, but also energy[2]. This is particularly important in the case of remediation of polluted sites, wastewater or gases, because, up to now, no attention has been paid to the sustainability of these processes, and they were proposed, developed and evaluated just to solve the environmental issue aimed, without considering the deep implications that they may produce on the consumption of resources or energy, and that may decrease its environmental considerations, when they are analysed from a globalized point of view[3-6]. Because of that, environmental electrochemical technologies, a variety of environmental remediation processes that aims to treat wastewater, soil and polluted gases using electrochemical reactions, is appearing as a very promising choice, because in this set of technologies, the electricity is the primary and almost exclusive necessity and, consequently, the impact on consumption of resources is minimized with respect to other non-electrochemical technologies[7], exhibiting lower carbon dioxide and water fingerprints. These promising features have been stated in recent works, in which life cycle assessments have been applied to these technologies. These works demonstrate that their sustainability rely on the sources of energy available. As well, they indicate that, regardless of the sources used, these technologies compare very favourably with other technologies which are currently in full scale applicability [8].

This good sustainability perspectives are intensified when electricity powered to the electrochemical devices is provided by renewable sources. This has been clearly stated in a recent authoritative review focused on the powering with green energies of electrochemical devices [9]. Thus, there are many sources of electricity that can be used to power electrochemical processes, but recent progress in solar photovoltaic and windmill technologies has been very important and now both technologies are becoming competitive with respect to other sources of energies. They exhibit an additional advantage in their use as sources of power for electrochemical processes: they can be applied in polluted places where electricity grid is not present, in a very easy and economical way, by implementing portable solutions that can be

more cost-effective than conventional applications. As well, they can be easily dismantled once the remediation is completed and assembled again in a new site.

However, the production of energy with both renewable sources (solar light or wind) depends on weather patterns that do not fit well with the energy demand and efficient energy storage devices are required for obtaining an efficient implementation[8,10]. Previous works have shown that direct application of renewable energy to wastewater and soil remediation is not as efficient as that provided by a regulated system[8,11], being this fact even more important in the case of soil remediation where the electrokinetic transport attained during sunlight with solar PV energy can be reverted overnight by back diffusion transport, leading to inefficiencies that are not caused by the technology itself, but by the way of powering it.

2. Setting energy storage using hydrogen technology to environmental processes

Fitting production of green energies and demand is a common problem in many applications of these types of green energies[12-15]. It is not an easy task and it may be faced through policies of use of electricity (changing prices of electricity during the day to promote the use of electricity in the valley demanding periods and penalize the use in demanding peaks) or by different technology approaches[16,17]. In this context, where various storage methodologies compete for prominence, the use of electrochemical technology has become crucial. This comprehensive technology ranges from integrating electrolyzers and fuel cells to various battery types, with a specific focus on redox flow batteries. Identified as promising candidates since their discovery, redox flow batteries offer high scalability, an extended lifespan, and adaptability to diverse storage needs[18,19]. Despite these promising attributes, electrochemical technology, particularly in the form of redox flow batteries (RFBs), has not yet reached full maturity. Substantial gaps persist, necessitating further research to identify a definitively advantageous solution. As the urgency for efficient energy storage solutions intensifies daily, the exploration of alternatives becomes increasingly imperative. Among potential replacements for conventional batteries, the integration of electrolyzers and fuel cells, especially those leveraging hydrogen, emerges as a compelling contender[20-22]. This approach offers advantages such as versatility and efficiency, seamlessly combining energy production and storage within a single device. However, like redox flow batteries, this alternative presents challenges related to complexity and elevated implementation costs[15,23]. This technology is appealing due to its capacity to improve hydrogen storage as a crucial energy vector[24-30]. This hydrogen-assisted energy-storage technology consists of the electrolysis of

water with the surplus energy obtained by the renewable source, the storage of the hydrogen produced and the production of electricity when needed using fuel cell technology[31,32]. Reactions occurring in the anodic and cathodic compartments of a proton exchange membrane (PEM) electrolyzer are represented by equations 1 and 2, respectively[33,34]. Alternatively, an anionic membrane, instead of the proton exchange membrane, can be used in a modification of this technology that operates in alkaline media (alkaline electrolysers) and that is appearing as a very promising option nowadays[35,36].

$$H_2O \rightarrow 0.5\ O_2 + 2H^+ + 2e^- \quad [1]$$

$$2H^+ + 2e^- \rightarrow H_2 \quad [2]$$

Although the applicability of these technologies is very promising with technology readiness level (TRLs) that in the first case are near to the highest (TRL 9), there are some flanks that should be overcome in their application to environmental processes and that include:

1) the efficient storage of hydrogen, which is committed by the extremely low volumetric energy efficiency of hydrogen, in turn associated to the very low molecular weight of hydrogen, and that makes necessary the installation of large high-pressure hydrogen storage tanks and limits, as well, the extension of the regulation time down to just a few hours of energy storage capacity.
2) the management of water in places where there is a lack of this resource. Unfortunately, because of the climate change, many regions of the world are being affected by a desertification process and providing high quality water is becoming a serious problem, because it implies the application of reverse osmosis or electrodialysis to produce a high quality water stream, ready to be used in electrolysers, and a rejection stream that should be reintroduced into the environment and that may contribute to the salination of reservoirs. In fact, the environmental viability of many real projects is being frightening in many regions, being this topic of particular interest in mediterranean countries such as Spain, where specialists in water management are strongly concerned about finding suitable ways to reach a sustainable solution for this unexpected problem.
3) the necessity of operation out, and sometimes far, of an industrial environment, with lower availability of auxiliary services and the convenience of the design of portable solutions that can be assembled and dismantled easily, minimizing the implementation of non-strictly needed operations or processes.

Among these problems, the management of water is arising as a very limiting process that commit the green labelling of these technologies. Use of a less exigent water electrolysis

technology (from the viewpoint of water management) is a really interesting possibility, worth of being studied. In this point, the chlor-alkali electrolysis technology may appear as a good alternative because, among many other factors[37-41], in this case the necessities of high purity water are lower as the feedstock is a brine of sodium chlorine (<50 g/L), although it can also operate with saline water (30<[NaCl]<50 g/L) or, even, with brackish solution (0.5<[NaCl]<30 g/L). This opens the possibility of using the alternative set of reactions shown in eqs. 3 and 4, for which high quality water is not required and that provides not only hydrogen but also caustic soda and chlorine as side products[42]. Both chemicals have many applications and their industrial production, in the well-known electro-intensive chlor-alkali industry, is frightened by the huge increase in the cost of electricity.

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad [3]$$

$$2H_2O + 2Na^+ + e^- \rightarrow H_2 + 2\,NaOH \quad [4]$$

The chloride electrolyzers, responsible for converting electrical energy into chemicals, are well known, as they are used in the important chlor-alkali industry[43-46]. They are currently at the maximum Technology Readiness Level (TRL) of 9 (actual system proven in operational environment), because they are already in-use in this industry for decades, although improvement in the process as still possible, especially with the development of new electrodic coatings[44,47]. Since the last quarter of the twentieth century, it is well known that, for this technology, the use of Mixed Metal Oxide (MMO) electrodes, with ruthenium oxides in the formulation (typically coating of TiO_2 and RuO_2 on a titanium support, so-called Dimensionally Stable Anodes by the company De Nora, that holds the industrial property of the most famous and applied coating, the DSA®), is the best option. In fact, their development was a turning point in the chlor-alkali process due to their very high efficiency and stability. The cathode is less important and typically stainless steel or Raney Nickel are used, looking for stability and reduction in cell voltage, and a cation exchange membrane is required to separated anodic and cathodic compartments, preventing the disproportionation of chlorine with the caustic soda. Operation current densities are around 300-500 mA cm^{-2} when the electrolyzer is fed with a brine solution, for which a cell voltage in the range 3.0-3.6 V is typically obtained. Worth to take in mind at this point is that optimum current densities are also different in other industrial chlor-alkali processes, currently in disuse, like the quicksilver technology in which 800-1300 mA cm^{-2} is the optimum range (3.9 - 4.2 V) and the diaphragm technology (90-260 mA cm^{-2}, 2.9 - 3.5 V) [11]. However, the membrane process is, nowadays, the most important process,

and it is classified by European Union authorities as best available technology in the official Best Available Technologies References documents (BREF) [48,49].

On the other hand, the fuel cells are responsible for the conversion of chemicals into electricity, and those based on the reduction of chlorine are in a much more incipient state as compared to the chlor-alkali electrolyzers[50-53]. In fact, their TRL is not 9, like in the case of the industrial electrolyzers, but much lower: in fact, a TRL of 4 may be even too high to define its current position nowadays. These electrochemical cells aim to produce electrical energy by reducing chlorine and oxidising hydrogen to produce a stream of hydrochloric acid. An important point to be considered is that chlorine is known to be a much stronger oxidant than oxygen, which can be an advantage for fuel cell operation by reducing reliance on platinum. However, the corrosion associated to its use should have a major impact on the service lifetime of the materials, in particular of membranes[54,55]. This technology immaturity makes interesting the critical comparison of the use of chlorine and oxygen as comburent in fuel cells because the use of oxygen (including air) may have the advantage of simplicity and durability of components, and this fuel cell technology is currently at TRL of 9. This fact, together with the extremely large number of cost-effective applications of chlorine, with a higher demand and price than hydrochloric acid, means that the chlorine commercialization could have a great interest.

3. Looking for the chlor-alkali reversible electrochemical cells technology

Despite electrolytic chlor-alkali technology is currently at the highest technology readiness level (TRL) of 9, and there is no gap for a significant research in the development of more efficient cells after several decades of application in industry (no breakthrough findings can be expected), the application of chlor-alkali technology in a reversible way, that is using chlor-alkali technology to produce hydrogen from surplus energy and regenerate again electricity using hydrogen and chlorine (or oxygen), needs for the evaluation of new efficient electrode coatings and novel electrochemical cells concepts, as well as of the fixation of milder operation conditions than in the chlor-alkali industry, because:

1. the facilities for an energy storage device of limited size are not going to be as wide-ranging as those found in conventional chlor-alkali factories and, consequently, they should be conceived and designed in a more portable way, without considering the existence of the same auxiliary equipment. As well, the feedstock used does not have to be a concentrated brine and the purification of output streams should be not considered as exigent from the quality point of view as in this industry.

2. the chlor-alkali fuel cell technology is currently in its beginning with very few published works [56], and an excessive number of patents (due to the potential importance of the results) without proven results, as it is often the case in this field in which an idea or concept is firstly patented and then developed, or not, depending on economic interests.

That is, energy storage using chlor-alkali technology means:

1. a redefinition of the standards used nowadays in chlor-alkali industry, especially when this storage is aimed to power environmental electrochemical processes in which the size of the application is going to be very limited. As well, operation at the lowest temperature will be the target for the sake of simplicity, trying to minimize heating or cooling operations. Also, easy facilities that avoids complexity and additional process lines: the human power must be minimized because the main target is not the industrial production but the environmental remediation.
2. Fixing how hydrogen can be reverted into electricity with the development of chlor-alkali fuel cell technology or, alternatively, with more conventional fuel cell technology involving the use of oxygen as comburent and the valorisation of chlorine and caustic soda as valuable resources in the context of circular economy. This means the consideration of efficiency not only in terms of energy use but also in the globalized context of circular economy.
3. The integration of processes with single reversible cell trying to minimize investment costs or the design of two specialized cells (one as electrolyzer and other as fuel cell) trying to increase efficiency is also worth of evaluation.

4. Towards new concepts of chlor-alkali electrolyzers

Differences between the necessities of chlor-alkali technology for industrial production of commodities and energy accumulation has been started to be faced recently, by comparing the performance of reversible cells equipped with electrodes containing different coatings and operated at room temperature[57-62] at current densities not only in the same range of that used in the chlor-alkali industry, but also in lower ranges (from 100 up to 660 mA cm^{-2}), that facilitates operation in much smaller devices and with the evaluation of the powering of this technologies with green energies[61]. In these works, two types of electrolyzers were compared (Figure 1) for which the main difference is the way in which the membrane was used: as a simple separator of compartments (Prototype 1) or as an electrolyte being integrated into a Membrane Electrode Assembly (MEA) (Prototype 2). In both cases the compartments are fed

with liquids in this electrolyzer mode, although both concept-cells are also evaluated as fuel cells. Table 1 compiles the main characteristics of the tests made for the comparisons and the resulting values reached in the two main outputs evaluated: the efficiency in the cathodic production of hydrogen and the ratio between the anodic production of chlorine and that of oxygen, outputs that fixed the effectiveness of the different electrolytic technologies evaluated[56-59,62]. With respect to the production of hydrogen, current efficiency is within the range 57.6-97.7 % (maximum theoretical production is 18.65 mmol H_2 Ah^{-1}). Lower values are explained in terms of a very important chlorine crossover, confirmed experimentally, and that makes hydrogen production competes with the reduction of hypochlorite in the cathodic chamber. Damages in the membranes by the strong oxidizing capacity of chlorine were also highlighted in other works[50,52,53] and may become in one of the main handicaps in this technology, especially when reversibility and integration is looked for.

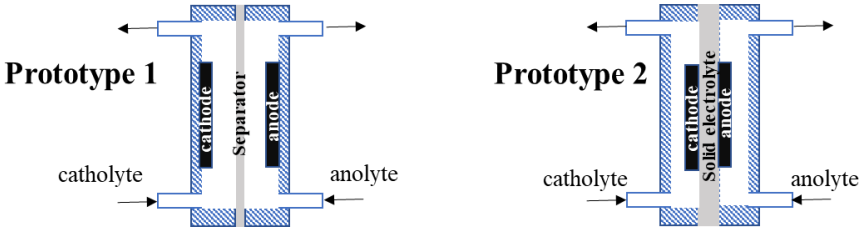

Figure 1. Scheme of the prototypes evaluated for application of the chlor-alkali energy storage.

Formulation of the coating of the electrodes is an important factor, particularly the value of the Ru/Pt ratio. Thus, this influence is shown in Figure 3a, where a better performance can be observed when the electrolysis operated under soft conditions (100 mA cm^{-2}) instead of harsh conditions (7.4 V). Regarding hydrogen production efficiencies, better performances are obtained working in the range 3-4 (18.18 ±0.04 mmol H_2 Ah^{-1}) and values higher than 4 nearly halves this efficiency (10.74 mmol H_2 Ah^{-1}).

Table 1. Main operating conditions applied in the electrolyzer and results obtained.

Cl_2 electrode	H_2 electrode	Electrode area / cm^2	Prototype	Anolyte	Catholyte	T / °C	E / V	j / mA cm^{-2}	W_{op} / W cm^{-2}	η / mmol H_2 Ah^{-1}	Cl_2/O_2 ratio	Ref.
$Ru_{0.2}Ti_{0.6}O_2Pt0_{.2}$ on Ti plate	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1	2.0 M NaCl	2.0 M NaCl	25	7.4	459.75	3.40	16.06	3.74	[57]
							3.46	100	0.346	15.82	1.86	
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti plate	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1	2.0 M NaCl	2.0 M NaCl	25	7.4	473.33	3.50	13.48	4.79	[57]
							3.60	100	0.36	18.22	3.32	
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti foam	Pt/C on carbon paper		2				4.40	100	0.44	15.57	6.22	[62]
$Ru_{0.4}Ti_{0.5}O_2Pt_{0.1}$ on Ti plate	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1	2.0 M NaCl	2.0 M NaCl	25	7.4	404.20	2.99	17.82	2.38	[57]
							3.47	100	0.35	18.14	3.31	
$Ru_{0.45}Ti_{0.5}O_2Pt_{0.05}$ on Ti plate	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1	2.0 M NaCl	2.0 M NaCl	25	7.4	660.86	4.89	15.62	2.42	[60]
							3.70	100	0.37	10.74	3.16	
$Ru_{0.3}Ti_{0.7}O_2$ on Ti foam	Pt/C on carbon paper	2	2	2.0 M NaCl	2.0 M NaCl	25	4.23	100	0.42	14.96	7.10	[62]
$Ru_{0.5}Ir_{0.5}O_2$ on Ti foam	Pt/C on carbon paper		2	2.0 M NaCl	2.0 M NaCl	25	4.01	100	0.40	12.96	3.06	[62]

Regarding the selectivity in the production of chlorine, higher ratios attain ratios chlorine/oxygen always

over 3, reaching a value of 4.79 for the formulation $Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ and it is also highlighted than iridium oxides promote the oxidation of water over chlorides (ratio chlorine /oxygen decreased from 6.22 to 3.06 when these oxides were used) and that platinum also promotes the formation of oxygen, reaching the electrode without platinum an outstanding ratio chlorine/oxygen of 7.10. Regarding the effect of the type of electrochemical cells, Figure 3b demonstrates that Prototype 1 outperforms Prototype 2 in terms of hydrogen production efficiency (15.73 ±2.50 mmol H_2 Ah^{-1} vs 14.50 ±1.02 mmol H_2 Ah^{-1}) but it undergoes a 18.3 % higher chlorine crossover as it is demonstrated in the comparison of the average differences between production of hydrogen and chlorine (1.44 ±0.69 mmol Ah^{-1} vs 0.26 ±0.14 mmol Ah^{-1}) and obtain a less favourable chlorine/oxygen ratio. Regarding energy consumption, Prototype 1 needed lower cell voltages to reach the same current density than Prototype 2 (3.54 ±0.083 V vs. 4.22 ±0.098 V for 100 mA cm^{-2}), which means that energy is more efficiently used when the membrane is only used as a separator (lower exergy).

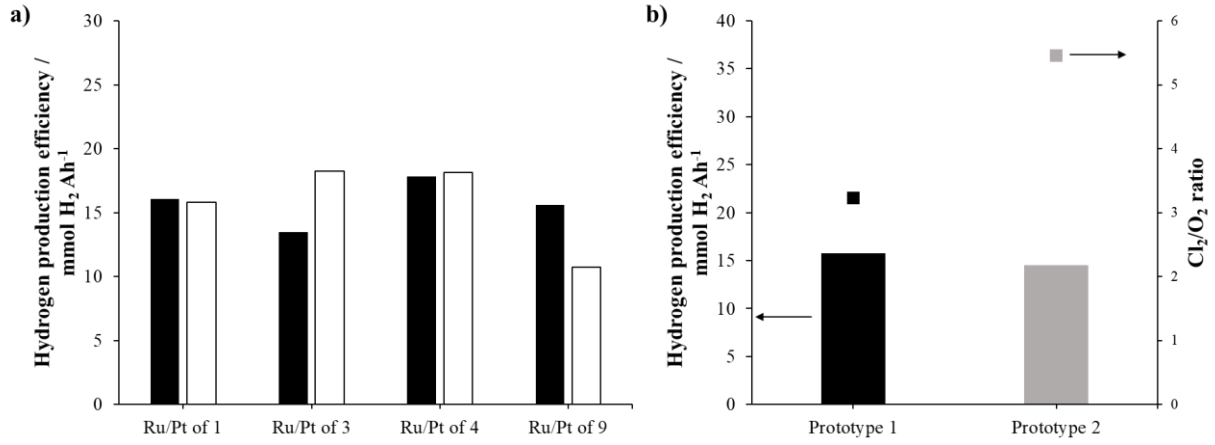

Figure 3. a) Influence of the Ru/Pt ratio in Prototype 1a on hydrogen production efficiency, and b) influence of the prototype type on hydrogen formation efficiency and anodic chlorine/oxygen formation. Black bar: electrolysis at 7.4V; white bar: electrolysis at 100 mA cm^{-2}.

The cells used in those studies were not as optimized, from the mechanical design and manufacturing point of view, as industrial cells currently used in the chlor-alkali industry (current collectors, heat dissipation, etc), and cell voltages can be easily decreased in a future evaluation carried out at a larger TRL. However, comparative results obtained in those studies are interesting because they are compared in the same conditions and allow to reach sound conclusions. Therefore, both types of electrochemical cells have advantages and disadvantages,

and it is not clear which is the best candidate for being applied in energy storage for environmental process powering.

5. Performance of chlor-alkali fuel cells at environment temperature

As previously explained, the main weaknesses of the reversible chlor-alkali electrochemical technology for energy storage are expected on the development of the fuel cell. Although the best results in energy production from H_2 (gas) and Cl_2 (gas) are expected in PEM fuel cells fed with gaseous comburent and fuels, the use of liquid feedstock is also considered of interest in the search of a unique reversible electrochemical cell. Table 2 compiles the main figures of merit obtained from the same studies used for comparison purposes in previous section of this critical review[57-62], using the same two reversible electrochemical cells, adapted to different types of feeding as indicated in Figure 2 (prototypes 1a and 1b with membrane as separator and prototypes 2a and 2b with membrane integrated into a MEA).

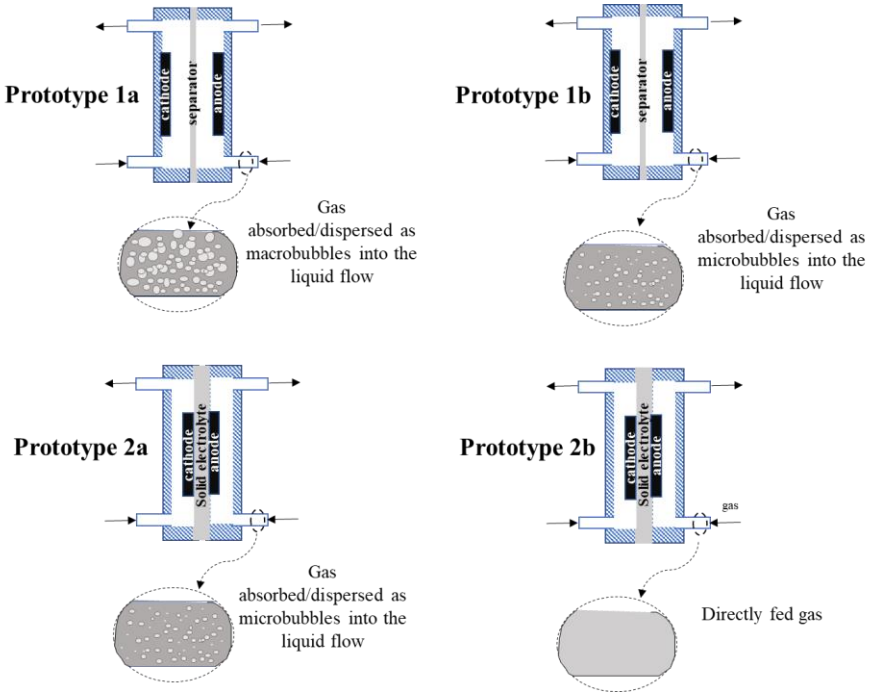

Figure 2. Prototypes of fuel cell for the chlor-alkali process.

The difference between the two prototypes 1 lies in the variation of the size of the gas bubbles absorbed in the liquid. Bubbles in prototype 1a were coarser, whereas in prototype 1b, they were characterized by being finer. On the other hand, Prototype 2a was fed with gas dissolved in the form of microbubbles into the liquid flow, while Prototype 2b was characterized by being directly fed with the gas.

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Table 2. Main operating conditions applied in the fuel cell and results obtained.

Cl_2 electrode	H_2 electrode	Electrode area / cm^2	Prototype	Anolyte	T / °C	E / V	j / mA cm^{-2}	W_{op} / W cm^{-2}	W_{max} / W cm^{-2}	η / Ah mol^{-1} H_2	OCV / V	Ref.
$Ru_{0.2}Ti_{0.6}O_2Pt_{0.2}$ on Ti	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1a	2.0 M NaCl	25	0.5	2.04	3.40	1.02	12.25	1.35	**[57]**
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1a	2.0 M NaCl	25	0.5	2.46	0.34	1.24	9.18	2.00	**[57]/ [58]**
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1b	2.0 M NaCl	25	25	4.82	3.50	1.18	4.26	1.41	**[58]**
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti foam	Pt/C on carbon paper	2	2a	2.0 M NaCl	25	0.5	7.59	0.36	3.58	4.95	1.36	**[58]**
$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$ on Ti foam	Pt/C on carbon paper	2	2b	2.0 M NaCl	25	0.5	9.68	0.44	2.36	12.53	1.82	**[58]**
$Ru_{0.4}Ti_{0.5}O_2Pt_{0.1}$ on Ti	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1a	2.0 M NaCl	25	0.5	2.96	2.99	1.48	17.27	1.29	**[57]**
$Ru_{0.45}Ti_{0.5}O_2Pt_{0.05}$ on Ti	$Ti_{0.8}Pt_{0.2}$ on Ti	2	1a	2.0 M NaCl	25	0.5	1.90	0.35	0.95	23.31	1.38	**[57]**
$Ru_{0.3}Ti_{0.7}O_2$ on Ti foam	Pt/C on Carbon paper	2	2a	2.0 M NaCl	25	0.5	3.14	1.65	1.05	6.96	0.52	**[62]**
$Ru_{0.5}Ir_{0.5}O_2$ on Ti foam	Pt/C on Carbon paper		2a	2.0 M NaCl	25	0.5	4.00	3.33	1.77	9.08	0.59	**[62]**

As seen, efficiencies range from 4.26- 23.31 Ah mol^{-1} Cl_2 (17.2-48.8%, considering the maximum attainable value of 53.2Ah mol^{-1} Cl_2). High values of Ru/Pt ratio exhibit a positive effect on the performance of the fuel cell and improve efficiency in the transformation of chlorine into electricity. However, a ratio of Ru/Pt of 4 makes better the operation power density reaching values in the nearness of 1.4 mW cm^{-2}.

In comparing prototypes type 1 (membrane as separator) with type 2 (membrane within a MEA), Figure 4 shows that the average values of current density exerted are higher for type 2 (6.20 ±2.53 mA cm^{-2} vs 2.84 ±0.84 mA cm^{-2}), because of the higher ohmic loses associated to their larger interelectrode gap, although these prototypes reach a higher efficiency in the production of electricity (13.25 ±5.63 Ah mol^{-1} Cl_2 vs 8.38 ±2.43 Ah mol^{-1} Cl_2).

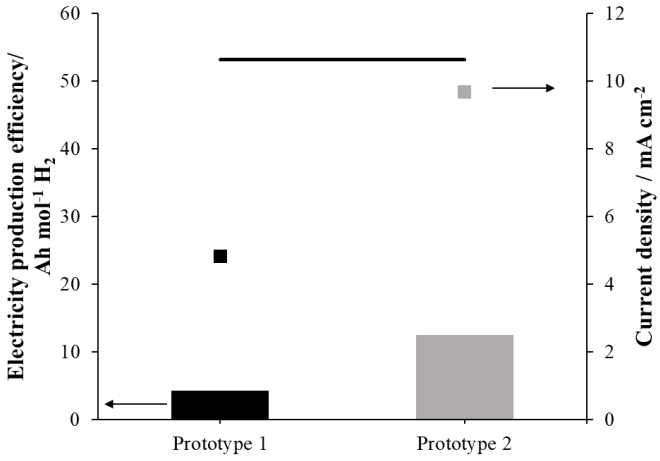

Figure 4. Comparison of the performance between Prototype 1 and Prototype 2 in terms of current density obtained and electricity production efficiency per mol H_2 consumed. Black point: Prototype 1; white point: Prototype 2; black line: maximum electricity production in terms of H_2 consumed.

On the other hand, Figure 5 shows results obtained in the fuel cell with the different prototypes (1a, 1b, 2a and 2b). The differences between prototypes 1a and 1b are based on the bubble size, and despite Prototype 1b integrates a special mechanical device that generates a much lower average bubble size, it reaches poorer performance (4.26 Ah mol^{-1} Cl_2 vs 15.50 ±4.79 Ah mol^{-1} Cl_2). Regarding the use of liquid or gas hydrogen streams as feedstock (which cannot be made with prototypes without MEA because the solid electrolyte is required to provide a flux of ions between electrodes when feeding gas streams), prototypes 2b compares favourably with 2a in terms of efficiency (4.95 vs 12.53 Ah mol^{-1} Cl_2) and energy produced (6.22 vs.3.05 W cm^{-2}), highlighting the better performance of the system fed with gas.

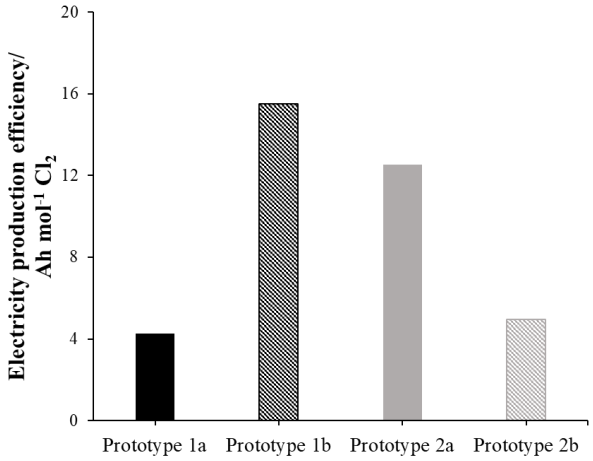

Figure 5. Maximum electricity production efficiency per mol Cl_2 consumed in each prototype.

Thus, for the operation as chlor-alkali reversible cells, there are two possibilities of operation working in reversible mode: using a cell in which the cell is divided in two compartments by a membrane, feeding both compartments with liquid solutions in both operation modes (electrolyzer and fuel cell) in which hydrogen is supplied as a dispersion of bubbles in an electrolyte or using a cell provided with a MEA, that it is fed with liquid solutions during electrolysis and in the case of operation in fuel cell mode with gaseous hydrogen. It is important to realize that all devices discussed may work in reversible mode, pointing out that, the same cell can be used as electrolyzer and fuel cell which is an advantage in terms of simplicity. As well, at this point it is important to consider that the integration of the two electrochemical processes in one single process can be worse than the operation of two separate cells: one as electrolyzer (where Prototype 1a seems to slightly overcome the rest of prototype tested, especially if membranes with lower crossover are obtained) and other as fuel cell (where Prototype 2b is clearly advantageous). Anyway, considering that fuel cell stage may become the bottleneck of the technology, more efforts were concentred in the MEA option as it was found to perform better in this fuel cell operation mode.

6. Is it advantageous the operation of chlor-alkali fuel cell at higher temperatures?

Operation at environment temperature takes advantage of the use of easier setups and this is one of the important requisites looked for in a portable energy storage device for being used to regulate power in environmental applications. However, temperature affects the kinetics of the electrochemical processes and, although is not as important in electrolyzer than in fuel cells, chlor-alkali electrolysers operated in industry always near the boiling point of water to take advantage of this improvement in kinetic performance. Nevertheless, results shown in previous

sections about performance of electrolyzers indicates that it is feasible operation at much lower temperatures and suitable efficiencies are obtained with softer equipment necessities. However, the main impact of temperature is expected to be found in fuel cell operation and Table 3 shows performance above environment temperatures, both below and above water boiling point, which is a critical point in fuel cell technology. In Figure 6, the performance of the fuel cell when operated at low temperatures (up to 80ºC) and high temperatures (from 120 to 160 ºC) is shown. In the first case (Figure 6a), results indicate that not only the hydrogen but also the chlorine streams fed to the fuel cell needed humidification and 60 ºC was the best operation temperature from the viewpoint of efficiency. However, the extreme effect of the humidification makes that a better selection was to operate at 25 ºC, where a value of the average operating current density of 8.98 ±0.43 mA cm^{-2} at 0.5 V allowed to reach a power density of 6.97 ±0.06 mW cm^{-2} and a good efficiency of 38.09 ±5.04 Ah mol^{-1} Cl_2 (faradaic efficiency of 71.6 %). Operation at temperatures above 100 ºC required to use membranes adapted to operation at high temperatures and also to adapt the electrode coating to this membrane[63]. In this case (Figure 6b), the best operation was obtained at 120 ºC with a standard coating of $Ru_{0.75}Pt_{0.25}$/C, for which operation at 0.5 V yielded 94.11 mA cm^{-2}, 47.05 mW cm^{-2} and 55.23 Ah mol^{-1} Cl_2. These results were better than those obtained operating at lower temperatures. However, it was found that durability of the MEAs hardly overcomes the duration of one-two tests, indicating that chlorine affected seriously to materials when it is operated at high temperature.

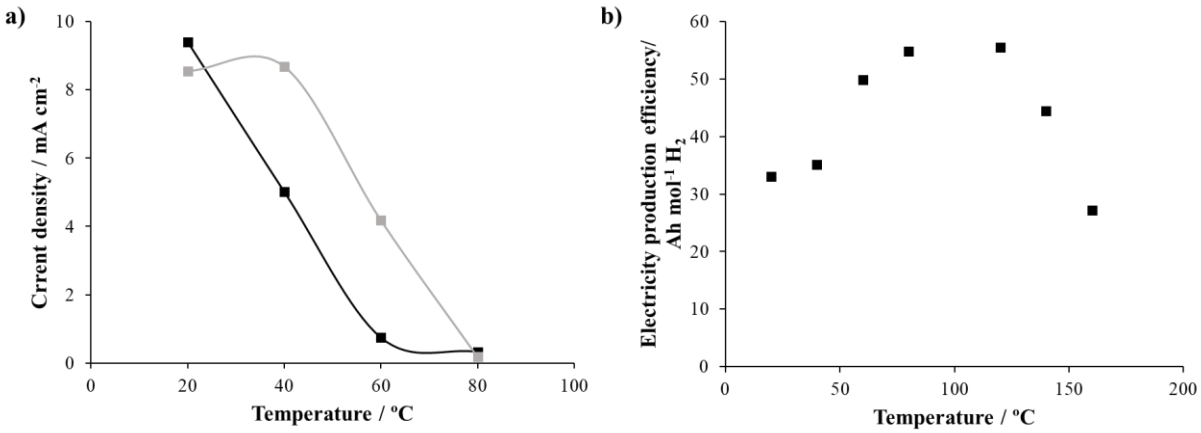

Figure 6. a) Maximum current density produced in the fuel cell at low temperature, and b) comparison of the fuel cell performance in terms of electricity production efficiency. Black point: Non-humidified; grey point: humidified chlorine

Table 3. Main operation conditions applied in the high-temperature fuel cell and results obtained.

Cl_2 electrode	**H_2 Electrode**	**Electrode area / cm^2**	**Prototype**	**Anolyte**	**Catholyte**	**T / °C**	**E / V**	**j / mA cm^{-2}**	**W_{op} / mW cm^{-2}**	**η / Ah mol^{-1} H_2**	**OCV / V**	**Ref.**
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b	Humidified H_2 gas	Non-humidified Cl_2 gas	20	0.5	9.41	7.03	33.05	1.14	[59]
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			40		5.02	4.58	35.20	1.11	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			60		0.75	1.57	49.92	1.38	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			80		0.33	0.21	54.86	1.50	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b	Humidified H_2 gas	Humidified Cl_2 gas	20	0.5	8.55	6.90	43.13	1.13	[59]
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			40		8.68	3.23	68.44	1.08	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			60		4.18	0.14	77.06	1.14	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C on carbon paper	25	2b			80		0.18	2.43	34.82	1.16	

Table 3. Main operation conditions applied in the high-temperature fuel cell and results obtained.

Cl_2 electrode	H_2 electrode	Electrode area / cm^2	Prototype	Anolyte	Catholyte	T / ºC	E / V	j / mA cm^{-2}	W_{op} / mW cm^{-2}	η / Ah mol^{-1} H_2	OCV / V	Ref.
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C	25	2b	Non-humidified H_2 gas	Non-humidified Cl_2 gas	120	0.5	94.11	47.05	55.23	1.05	[60]
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C	25	2b			140		15.55	7.78	44.47	0.70	
$Ru_{0.75}Pt_{0.25}$/C on carbon paper	Pt/C	25	2b			160		17.82	8.91	27.25	0.97	
$RuCl_3$/ H_2PtCl_6 without thermal treatment on carbon paper	Pt/C	25	2b	Non-humidified H_2 gas	Non-humidified Cl_2 gas	120	0.39	20	7.8	31.68	1.00	[60]
$RuCl_3$/ H_2PtCl_6 without thermal treatment on carbon paper	Pt/C	25	2b			140	0.48		9.6	50.69	0.82	
$RuCl_3$/ H_2PtCl_6 without thermal treatment on carbon paper	Pt/C	25	2b			160	0.46		9.2	48.22	0.78	
$RuCl_3$/ H_2PtCl_6 without thermal treatment on carbon paper	Pt/C	25	2b			180	0.36		7.2	48.03	0.75	
Pt/C on carbon paper	Pt/C	25	2b	Non-humidified H_2 gas	Non-humidified O_2 gas	120	0.32	60	19.2	45.78	0.79	[60]

7. Is it worth to use chlorine as a comburent or is it more convenient to sell or apply it as reagent?

Electro intensive industries are suffering from the impact of the extremely important increase in the cost of electricity, experienced in the recent years, that it is frightening its own survival. In fact, primary production of aluminum and chlor-alkali productions are in danger in many countries. At this point, the use of chlor-alkali technology for energy storage and, in particular, in environmental processes, could be seen as chance for these companies, because they can produce chlorine and caustic soda as byproducts in electricity regulation stations for free (without paying for the electricity), instead that in conventional factories where they should pay for the electricity. This means that even processes with much lower efficiencies could be welcome. In addition, chlorine and caustic soda have many applications in environmental technologies including uses in the electrochemically assisted technologies. Among them, the use as disinfectants of tap water and as oxidants of inorganic pollutants are worth to be highlighted for chlorine, while the regulation of pH and, especially, the carbon dioxide fixation [64-69] are the most outstanding for caustic soda. Performance of PEM or AEM is widely evaluated in the literature, but this evaluation is not as wide in the case of high temperature fuel cells.

For this reason, it is interesting the comparison of the performance of a high temperature PEM fuel cell when oxygen is used instead of chlorine. Results shown in the literature [60] demonstrated that, although electrochemical performance with chlorine is better than performance with oxygen, using oxygen as comburent also allowed to obtain suitable outputs with current efficiency of 86.2 % when operating at 0.5 V (yielding 60 mA cm^{-2}, 19.2 mW cm^{-2} and 45.78 Ah mol^{-1} H_2). However, despite this lower efficiency, a clear advantage was reported: service lifetime of this approach is much higher. In fact, robustness of PEM technology has been widely evaluated in the literature in terms of prolonged service lifetime [70]. Opposite, currently service lifetime of chlorine fuel cell technology is much lower and at even the end of the short tests the MEA is always damaged, regardless of the operation temperature.

Considering all these facts, best alternative now for the application of a hydrogen-based energy storage system consist of coupling chlor-alkali electrolyzer, which a less exigent demand of water, and conventional PEM fuel cells fed with oxygen as comburent. All these technologies are now available at high TRL, and the distributed production of chlorine and caustic soda can

be a promising alternative either for application in environmental technologies (including electrochemically-assisted technologies) or even for commercialization.

8. Conclusions

This work points out the necessity of regulation of green energy to power electrochemically assisted remediation processes, indicating that in case of using hydrogen-based energy-storage devices the management of water is a serious issue that could be faced using chlor-alkali technology. There are important differences in the specification required for the implementation of chlor-alkali technology in industry and in energy storage. With the existing knowledge, it can be concluded that reversible electrochemical cells are not still mature for being used as competitive in hydrogen storage systems. Opposite, the chlor-alkali electrolyzer technology is suitable for this application and can be easily applied even at operation conditions not as optimized as those applied in industrial processes including room temperature and lower concentration of feedstock. This technology can be successfully combined with standard membrane fuel cell technologies which can be advantageous considering the high added value of chlorine as reagent within a context in which chlorine production in electro intensive industries is seriously frightening by the strong increase in the electricity cost and this can open the possibility of obtaining this valuable reagent as a side product.

Credit authorship contribution statement.

Iñaki Requena: investigation; methodology; and data curation; writing – original draft

Mireya Carvela: investigation; methodology; and data curation; writing – original draft

Carmen M. Fernández-Marchante: supervision; validation; formal analysis; and writing – review and editing.

Justo Lobato: supervision; validation; formal analysis; and writing – review and editing.

Manuel A. Rodrigo: conceptualization; supervision; formal analysis; and writing - review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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