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Back to the future with emerging iron technologies

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Here is a comprehensive overview of iron's potential in low-carbon energy technologies, exploring applications like metal fuel combustion, iron-based batteries, and energy-carrier cycles, as well as sustainable approaches for production and recycling with a focus on reducing environmental impact. Iron, with its abundance, safety, and electrochemical characteristics, is a promising material to contribute to a decarbonized future. This paper discusses the advancements and challenges in iron-based energy storage technologies and sustainable iron production methods. Various innovative approaches are explored as energy storage solutions based on iron, like advancements in thermochemical Fe–Cl cycles highlight the potential of iron chloride electrochemical cycles for long-term high-capacity energy storage technology. Additionally, the utilization of iron as a circular fuel in industrial processes demonstrates its potential in large-scale thermal energy generation. Sustainable iron production methods, such as electrolysis of iron chloride or oxide and deep eutectic solvent extraction, are investigated to reduce the carbon footprint in the iron and steel industry. These findings also show the importance of policy and technology improvements that are vital for the widespread use and recycling of iron-based tech, stressing the need for collaboration toward a sustainable future.

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1 Iron as a solution in emerging technologies for a decarbonized energy future

The concept of energy resilience is now becoming an increasingly important topic of discussion at many levels (*e.g.*, social, economic, technical, and political), highlighting the need for concrete solutions. The shift towards producing energy from renewable and low-carbon energy sources instead of fossil fuels has been agreed upon at the government and industry levels as the way forward for sustainable societal development. The development of environmentally friendly energy technologies and systems has become a global urgent task. The adoption of this concept will lead to an increase in the production of environmentally friendly or green applications, including energy-efficient buildings, electric vehicles, and technologies for generating and storing renewable energy. Due to the increasing inclusion of intermittent renewable energy sources in the grid energy mix, there is an inevitable need for energy storage solutions to support these developments. On the production side, more cost-effective and efficient photovoltaic panels and wind turbines, fabricated for more accessible end-of-life materials recycling, and an advanced power management system will be required to support this shift. The flip side of clean and renewable technologies is the high and constant demand for minerals and metals.[1] The depletion of metal and mineral resources is a potential concern that could impact the future production of clean and renewable technologies.[2] To date, iron and steel are the most recycled materials (*i.e.* steel has a recycling ratio close to 95%).[3] The end-of-life recovery rate varies among metals, *e.g.* it is over 50% for zinc, aluminum, gold, cobalt, copper, and manganese,[4] while it is less than 1% for indium and gallium and less than 5% for Li-ion batteries.[5]

Iron is the most commonly used metal, widely available compared to others, and has been an essential part of social development for more than 5000 years. Due to its abundance and relatively low cost, it is an attractive material for various industries. New technologies and applications will further increase the demand for iron. However, the major drawback of using iron is its current carbon-intensive production technology, which has negative impacts on the environment. This highlights the need for improved methods of iron production. Data show that the iron and steel industry is responsible for one-third of global industrial CO_2 emissions, with increasing trends in all countries.[6] The transition to a low-carbon energy future includes the iron and steel industry and requires radical innovation to address the current fossil fuel mode of production. This may include implementing new technologies and processes that are not only risky and expensive but also complex, requiring systemic development.[3] For instance, one intensively studied promising option is the reduction of iron ore with hydrogen. Although it is not an established industrial process yet, there are some breakthrough projects ongoing in this direction.[7–19]

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Iron has great potential for use in emerging grid energy storage technologies. As research and development efforts continue to improve the storage of available renewable energy, the use of iron in these applications is likely to increase. Lately, the iron-based electrochemical energy storage (EES) options have drawn a lot of attention for several reasons; they are economically affordable, recyclable, less toxic, rich in valent states, and redox behavior with good energy density and unique electrochemical characteristics. Even more, iron-based aqueous EES are highly mechanically robust and resilient.[20]

Iron can play a significant role in a low-carbon intensity energy future, particularly in the production of green hydrogen. Green hydrogen is considered a perspective energy carrier that can contribute to the reduction of CO_2 emissions and other environmental impacts. Hydrogen global demand is estimated to increase by 4–5% per year,[21] and for the European scenario, hydrogen has the potential to meet 5–20% of industrial energy needs.[22] In addition, the production of green hydrogen is a necessity not only for environmental reasons but also for economic and energy security and diversification. Among promising green hydrogen production approaches, that use iron as an energy carrier, are chemical cycles,[23,24] alkaline electrolysis cells,[25] and thermochemical water splitting.[26] Therefore, the iron and steel industry can play a vital role in the development of the hydrogen economy.

Metallic iron has great potential as a fuel or energy carrier, although research in this area is still in its early stages. Iron fuel has several advantages over conventional fossil fuels, including its high energy density, ease of transport and storage, and low cost. Additionally, iron fuel can be produced from existing iron resources (iron ore) and can be reused through recycling (scrap iron). In a future with an abundance of renewable and low-carbon energy, metal fuels, including iron, are important for their potential applications such as fuel additives in propellants,[27] energetic materials,[28] fuels in batteries, and recyclable electro-fuels.[29] Additionally, metal propellants such as iron powder have the prospect of being used for *in situ* resource utilization in future space missions.[30] However, there are currently limitations to its application in a clean energy distribution network because of the lack of efficient technologies for transferring chemical energy from metal fuels into electricity or mechanical energy for end-users. It is important to recognize that the implementation of clean energy technologies involves complex considerations, including environmental and social risks. Policy support plays a vital role in ensuring the widespread adoption and safe recycling of these technologies. By considering the environmental impact, promoting the circular economy, and implementing supportive policies, iron-based technologies can play a significant role in the transition towards a sustainable energy landscape.

In this paper, a selection of innovative applications of iron in emerging low-carbon energy technologies is discussed. The paper also reviews current approaches for low-carbon-intensive iron production and recycling. Finally, it presents perspectives on the management of evolving iron technologies and current trends in the research and application of iron-based technologies in academia and industry. The paper aims to provide a comprehensive overview of the current state and future potential use of iron for energy technologies.

2 Applications of iron in emerging energy low-carbon technologies

Iron is abundant, safe, and possesses impressive electrochemical characteristics as detailed in Table 1. It is significantly cheaper than nickel, lithium, zinc, and aluminum, and its abundance is greater than both lithium and nickel. Compared to other metals, iron's specific capacity surpasses zinc and nickel, although it is lower than aluminum and lithium. Its volumetric capacity is superior to zinc and magnesium, matches copper, and is just slightly below nickel and aluminum. Aqueous solutions of iron, zinc, nickel, and copper salts (chlorides, sulfates, nitrates, phosphates), can undergo electroreduction *via* cold electrolysis. In contrast, aluminum cannot be electroplated from aqueous solutions. Environmentally, iron excels with low toxicity and a high recycling rate, outperforming aluminum and zinc in these aspects.[35,36] These properties position it as a highly promising material for energy storage technologies, particularly for large-scale applications. However, the application of iron for metal anodes for aqueous rechargeable batteries in practice is still limited by passivation, parasitic hydrogen evolution reaction, and low energy efficiency.[37] Nevertheless, innovation in energy storage devices and the advancement of battery technology are exponentially increasing. A few relevant examples of iron-based chemical cycles as energy storage devices and recent developments in the EES field are discussed below and summarized in Table 4.

2.1. Fe–Cl_2 chemical cycles for hydrogen production

The Fe–Cl (thermo- and electro-) chemical cycles have several advantages, such as low cost, known chemistry, and availability of materials. However, they also have some disadvantages, including low energy efficiency which is affected by either a low yield of reverse Deacon's reaction for chlorine conversion to HCl[38] or the energy-consuming reduction of iron oxides. A recent example of both thermo- and electro-chemical cycles is a materially closed technological loop that employs the hydrogen evolution reaction between iron powder and HCl acid.[39,40] Under room temperature conditions, the metallic iron is oxidized with HCl acid. The reaction releases hydrogen from HCl molecules while producing $FeCl_2$ as a byproduct.

2.1.1. Thermo-electrochemical cycles. Thermo-electrochemical cycles for grid energy storage and examples of thermo–electrochemical cycles based on the reduction of Fe^{2+} ions in the ferrous chloride aqueous solution were patented[40] and presented by Luin and Valant.[41] In the reductive segment of this cycle, the grid energy is used to electrolyze concentrated $FeCl_2$ solution and deposit the metallic Fe on the cathode. The iron metal becomes the energy carrier and can be easily stored. Chlorine gas is evolved at the anode and directed to a reactor, where within the reverse Deacon process the hydrochloric acid is regenerated, ready for re-use in the oxidative segment. In the oxidative segment, which comes into play when energy demand

Table 1 Comparative properties of iron and other elements for energy low carbon technologies (EU Comission 2023 (ref. 31); Kania and Saternus;[32] EU Comission 2018 (ref. 33); Li *et al.*[34])

Element (electrons transferred)	Price per specific capacity ($ per mA h)	Planetary element abundance (%)	Price ($ per kg)	Specific capacity (mA h g^{-1})	Volumetric capacity (mA h cm^{-3})	Redox potential (V)	E-o-L recycling rate	Toxicity
Fe (2)	0.125	5.3	0.12	960	7557	−0.45	62%	Low
Fe (3)	0.08			1439	11 328			
Al (3)	0.92	8.2	2.73	2980	8046	−1.66	51%	Low
Li (1)	3.77	0.002	14.56	3861	2062	−3.04	<5%	Moderate
Zn (2)	3.81	0.004	3.12	820	5845	−0.76	45%	Medium
Mg (2)	8.87	2	19.56	2205	3833	−2.37	13%	Very low
Cu (2)	12.71	0.007	10.71	843	7558	+0.34	55%	High
Ni (2)	22.52	0.009	20.56	913	8136	−0.26	16%	High
Co (2)	29.87	0.003	27.15	909	8092	−0.28	22%	High

outstrips supply, the metallic energy carrier is reacted with hydrochloric acid to produce hydrogen on demand. A mol of H_2 is formed per a mol of Fe. Without any need for storage, the hydrogen can be directly supplied to the fuel cell for conversion back to electrical energy (or for combustion). The remaining saturated metal chloride solution can then be stored, making it readily available for re-use in the reductive segment for electrolysis.

The metal energy density can be calculated from the stoichiometry of the chemical processes described above and the crystallographic properties of the Fe crystal cell. The calculated energy density for Fe is 11.3 kW h L^{-1}, which by far exceeds any other energy carrier used in the current energy storage technologies even liquid fossil fuels (see Table 2). The energy efficiency of the cycle can be as much as 80% and the AC-to-AC efficiency 38% (taking into account the 50%-efficiency of fuel cells).

By using the Fe solid-state energy carrier, it is possible to avoid the expensive hydrogen compression or refrigeration and its storage in tanks. It can resolve the fundamental problems of current EES technologies because it exhibits a combination of unique characteristics such as high energy density, a small land footprint for the new storage stations, no geographical constraints for the storage plants, no emission or waste due to a closed working cycle and no self-discharge during long-term storage (Fig. 1). In addition, the storage and conversion segments of the technology can be decoupled. The electrical energy storage can be realized at a suitable location near the power generation, while the conversion back to electricity can take place at one or multiple locations elsewhere. This offers the possibility for a very long-distance energy supply without losses (*e.g.*, over deserts, over the sea to remote islands, *etc.*).

The importance of energy storage is undeniable, *e.g.* storing excess energy and thus reducing electricity production, reducing carbon emissions, and managing grid stability.[53] The required characteristics such as long lifetime, low cost, high density, and efficiency are not yet all met simultaneously in energy storage technologies, so caution should be taken when selecting them for a particular application. Although the outlook for the future is very promising, the challenges of these systems remain technological and economic. Technologically, they struggle with achieving high energy density, long lifetimes, and high efficiency.[54] Issues such as thermal management and material limitations also persist.[55] Economically, high initial costs, maintenance expenses, market and policy uncertainties, and difficulties in securing financing still stay in the way of widespread adoption.[56]

2.1.2. Thermochemical Fe–Cl cycle. Recently, thermochemical methods have gained attention mainly because of their low environmental impact and cost-effectiveness. By using clean or waste energy sources they can be integrated into sustainable energy systems.[57] These methods involve a closed material cycle, in which oxygen and hydrogen are produced from water within a sequence of reduction–oxidation reactions driven by thermal energy. These processes typically operate at high temperatures (500–2000 °C) using a combination of exothermic chemical reactions at low temperatures and

Table 2 Comparison of specific energy and energy density of the energy carriers used in the proposed storage technology with currently used technologies and gasoline

	Energy density [kW h L^{-1}]	Specific energy [kW h kg^{-1}]
Elemental Fe (calculated based on Atkins and de Paula 2010 (ref. 42))	11.3 (Fe oxidation with HCl yielding H_2) 16.1 (burning Fe powder to Fe_2O_3)	1.4 (Fe oxidation with HCl yielding H_2) 2.1 (burning Fe powder to Fe_2O_3)
Gasoline (Mazloomi *et al.* 2012 (ref. 43))	9.5	12.9
Hydrogen gas (atmospheric pressure)	~0.003 (Lanz *et al.*[44])	33.3 (LHV)
Compressed hydrogen gas (700 bar)	1.3 (Hirscher & Hirose 2010 (ref. 45))	39.4 (HHV)
Liquid hydrogen ($T =< -253$ °C)	2.2 (Hirscher & Hirose 2010 (ref. 45))	(Lanz *et al.*[44])
Hydrogen in hydrides (Abe *et al.* 2019,[46] Klopčič *et al.* 2023 (ref. 47))	1.6–6.2	0.4–6.2
Commercially available Li-batteries (Li-ion, Li-polymer) (Choi and Aurbach 2016,[48] Hamerr and van Niekerk 2015 (ref. 49))	0.2–0.7	0.1–0.3
Emerging battery technologies (Li–S, Li–air, Mg–air) (Hagen *et al.* 2015,[50] Kim *et al.* 2019 (ref. 51))	0.4–1	0.35–1.5
Flywheels (Ibrahim *et al.* 2008 (ref. 52))	~0.02	
Compressed air energy storage (Hameer and van Niekerk 2015 (ref. 49))	~0.01	
Pumped hydropower energy storage (Ibrahim *et al.* 2008 (ref. 52))	~0.001	

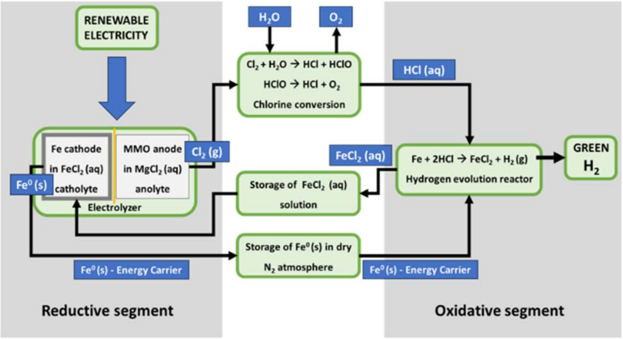

Fig. 1 Schematic material-flow diagram of the Fe-based power-to-solid EES technology.

endothermic reactions at high temperatures.[38] The thermochemical methods can either use only thermal energy or can be hybrid, utilizing both thermal energy and an additional energy source such as electricity.[58] The thermal energy required for these processes can be obtained through various means, such as concentrating sunlight, utilizing waste industrial heat, or electric heating. An example of reduction–oxidation reactions in the thermochemical cycles that produce hydrogen is the Fe^{2+} to Fe^{3+} back-and-forth conversions. One example of the chemical reactions involved in such cycles is shown in Table 3. Within these cycles, all materials are repurposed. In a modeling study of this cycle using Aspen Plus,[59] it was shown that the pressure has a negligible effect on reaction production rates, but increasing temperature favors oxygen and magnetite production while decreasing hydrogen production. Increasing the steam-to-chlorine ratio increases hydrogen, oxygen, and hydrochloric acid production.[59] Other types of the Fe–Cl cycles involve the oxidation–reduction reactions that occur between metallic iron and different iron species such as $FeCl_2$ $FeCl_3$, or different iron oxides.[26,61,62]

In the regeneration segment, $FeCl_2$ is thermally decomposed to yield HCl acid and iron oxide that is utilizing metallurgical processes reduced back to iron. The required low-temperature thermal energy for the decomposition processes can be obtained from industrial waste heat or concentrated sunlight as a renewable energy source.[62] This makes the process highly sustainable and ready to be integrated into clean energy systems. We conducted a life cycle assessment analysis (LCA) on this hydrogen production process, focusing on the operation phase. The detailed results will be presented in a forthcoming study. The operation phase included the use of water, heat, and electricity. Results comparing two scenarios (photovoltaic *vs.* grid electricity) show that the scenario using grid electricity has

Table 3 The reactions of an iron–chloride thermochemical four-step cycle for hydrogen production from Safari and Dincer[59] and Castro Oliveira *et al.*[60]

Steps	Reactions	
Thermal decomposition	$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$, $\Delta H^0 = -160.5$ kJ mol^{-1}	(1)
Reverse Deacon reaction	$Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$, $\Delta H^0 = +59.4$ kJ mol^{-1}	(2)
Hydrolysis	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$, $\Delta H^0 = +156$ kJ mol^{-1}	(3)
Chlorination	$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$, $\Delta H^0 = -244$ kJ mol^{-1}	(4)

Table 4 Considerations for the essential role of iron in emerging energy technologies

Technology	Maximum energy eff%	Key advantages	Key disadvantages
Redox flow batteries (RBFs)			
VRBF	87	High cycling stability High theoretical voltage, cost-effective	Species crossover, high costs, temperature sensitivity, electrolyte management, infrastructure requirements
ORBF	82	High energy density, environmentally friendly	Chemical instability, low solubility, degradation over time
Zn–Br RFB	85	High energy density, long cycle life	Bromine toxicity, potential for zinc dendrites
Zn–Ce RFB	71	High cell voltage (~2.4 V), lower cost compared to other RFBs	Limited stability, limited large-scale application, lowest energy efficiency
Iron redox flow batteries			
Fe RFBs	87	Scalability, longer cycle lives, non-toxic	Internal short circuits risk
Fe–Cl RFB	83	Eco-friendly, low cost	Low stability
Iron batteries			
Fe-air	94 after 1000 cycles	High energy density, cost-effective, environmentally friendly	Dendrite growth, longevity, anode passivation
Emerging iron batteries			
RCII	<80	Competitive reactivity, dynamics, energy density	Dissolution in acidic electrolytes, sluggish redox reaction
IHE	93	Stable lifetime (>20 000 cycles), cost-effective	Limited implementation
Battolyser	90	Dual-function (battery and electrolyzer)	Still under research and development

a significantly higher environmental impact than photovoltaic. This is evident in terms of abiotic depletion of elements and marine aquatic ecotoxicity potential (3 times higher), eutrophication potential, and ecotoxicity potential (2 times higher). Acidification potential and freshwater aquatic ecotoxicity show similar impacts in both scenarios. The analyzed process is sustainable and operates on a closed-loop principle, regenerating materials (iron and HCl) and requiring no additional raw materials. It can utilize intermittent renewable energy sources and act as a heat recovery system, producing a significant amount of green hydrogen. We refer to the preliminary studies conducted by Knoche *et al.*[63] and the comprehensive experimental studies conducted by Canavesio *et al.*,[61] which revealed that the Fe–Cl thermochemical cycle achieved a maximum energy efficiency of 37%, lower than the alternative cycles such as the Cu–Cl cycle with an efficiency of around 55%. The breakthrough in the implementation of Fe–Cl cycles might be achieved if the reverse Deacon's reaction could be replaced with a low-temperature catalytic process. In addition to the energy efficiency gains, the implementation of low-temperature catalytic processes would offer significant economic benefits. The reduced energy demand directly translates into lower operational costs. Moreover, the capital expenditure (capex) required for establishing and maintaining the Fe–Cl cycle system would also decrease, contributing to enhanced economic viability. The development of low-temperature catalytic processes would not only optimize Fe–Cl cycles but would also have important implications for industrial HCl production. Currently, vast amounts of hydrogen are consumed in the synthesis of HCl. By utilizing low-temperature catalytic processes, the hydrogen as a reactant would be substituted with hydrogen from water molecules, resulting in significant savings and making HCl production more cost-effective.

Challenges also involve chlorine management and corrosion prevention,[64] alongside the effective handling of reaction heat, $FeCl_3$ thermal decomposition kinetics, and hydrolysis of $FeCl_2$.[58] Due to the complexity of thermochemical cycles, studies on their simulation and performance at an industrial scale are limited.[65] Concerning environmental and safety risks, it is important to understand that very sophisticated and safe chlorine technology measures have already been developed and are required to be implemented in technology systems and processes involving chlorine or HCl.[66] The chlorine technologies must comply with the so-called Best Available Techniques (BAT) documents for chlorine management[67,68] and, if so, the environmental and safety risks are well under control. However, it is a fact that these measures make chlorine technology more expensive.

2.1.3. Electrochemical Fe–Cl cycle.

The iron chloride electrochemical cycle is based on the electrolysis of $FeCl_2$ aqueous solution. Energy is stored in the reductive–oxidative potential change Fe^{2+}/Fe by electro-reduction of iron cations from a concentrated $FeCl_2$ aqueous electrolyte, yielding metallic iron deposits on the cathode. Simultaneously, the evolved chlorine gas on the anode enters conversion to HCl acid through a reversed Deacon process.[69] Energy is released as hydrogen gas on demand through a spontaneous reaction between iron and

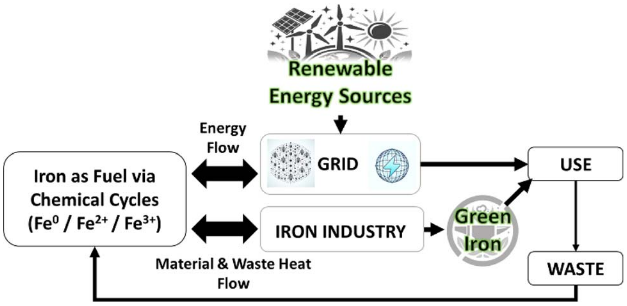

Fig. 2 Integration of iron chemical cycles into the iron industry and grid energy storage.

HCl acid. Iron and HCl acid can be stored stably for months, without self-discharge of stored energy. This makes the $FeCl_2$ electrochemical cycle. Suitable for long-term high-capacity energy storage technology.[40,41] Integrating iron chemical cycles within the iron industry and renewable energy storage systems for supporting the grid, as presented in Fig. 2, the potential of iron as a sustainable fuel source is highlighted.

2.2. Electrochemical energy storage using iron

Electrochemical energy storage (EES) systems play an important role in the utilization of renewable energy sources to balance the grid during energy fluctuations.[70] They can be implemented in stationary, portable, or transport applications. Aqueous rechargeable batteries using water-based electrolytes are promising alternatives due to their safety and potential to reduce production costs.[71]

2.2.1. Redox flow batteries (RFB). RFBs represent such an option for large-scale energy storage. RFBs have a range of unique chemistries, each with its distinctive features and challenges. Despite the numerous advantages, their widespread use is limited due to various obstacles. The hydrogen–bromine RFB (HBr RFB) chemistry, despite its potential as is the high-power density, struggles with corrosion issues. The corrosive nature of bromine can cause severe damage to the components, potentially limiting the longevity and efficiency of the system.[72] While the vanadium RFB excels in cycling stability, it poses significant environmental concerns due to its extensive use of vanadium electrolytes and the potential for leakage into groundwaters. Despite their advantages, high production and maintenance costs hinder the widespread adoption of vanadium RFBs, which must be addressed for large-scale energy storage viability.[73,74] China is leading with recent installations of 200 MW/800 MW h and 100 MW/500 MW h vanadium RFBs in Dalian and Hubei provinces.[75] In a related development, a vanadium–chromium RFB (V/Cr RFB) has been developed, combining the benefits of all-vanadium and iron–chromium systems. This system features a high theoretical voltage of 1.41 V and cost-effective chromium use, achieving a peak power density of over 900 mW cm^{-2} at 50 °C and stable performance over 50 cycles with over 87% energy efficiency, making it a promising candidate for large-scale energy storage.[76] Zinc–bromine RFB (Zn–Br RFB) uses a zinc bromide salt solution, and they are known for their high energy density and long cycle life.[77,78]

The organic RFB uses organic compounds as active redox species instead of metal ions. Their appeal comes from the wide range of potential organic molecules that could be used, which might provide higher energy density or more environmentally friendly options.[34] Aqueous hybrid organic–inorganic RFBs based on AQDS-ferrocyanide active materials have been used to highlight the main characteristics of ORFBs.[79] Research interest is growing in non-aqueous systems to pursue higher voltage output from RFBs, as conventional aqueous RFBs have a limit of the cell voltage window of 1.24 V. Non-aqueous organic RFBs exhibit other advantages, such as higher energy density, wider operating temperature range, faster reaction kinetics, and more combinations of organic redox couples.[80] However, organic solvents used in non-aqueous systems are known to have disadvantages such as volatility and toxicity.[81] The active organic species themselves can suffer from issues such as chemical instability, crossover through the membrane, low solubility, and degradation over time, which can negatively impact the performance and lifespan of the batteries.[82,83]

Zinc–cerium (Zn–Ce) batteries are a type of redox flow battery that uses cerium(III)/cerium(IV) and zinc for the redox couple. The Ce(III)/Ce(IV) and Zn(II)/Zn redox reactions take place at the positive and negative electrodes, respectively. Zinc–cerium batteries are known for their high cell voltage, high energy density, and lower cost compared to other redox flow batteries. Zinc–cerium RFBs are capable of providing one of the highest cell voltages (∼2.4 V) among flow batteries and a large theoretical energy density.[84] Another RFB chemistry is based on iron chloride (FeCl RFB). This type is well-regarded for its eco-friendliness and low cost. However, the most significant challenge for FeCl RFB is stability, which hinders its broader application in energy storage systems.

2.2.2. Iron redox flow batteries (Fe RFBs). In contrast, iron redox flow batteries (Fe RFBs) employ a distinct design with separate tanks for catholyte and anolyte. The energy storage capacity in Fe RFBs is determined by the volume of these tanks, making them highly scalable and ideal for utility-scale storage solutions. They typically exhibit longer cycle lives due to reduced degradation mechanisms. Moreover, while all-iron batteries are generally safe, they might face risks like internal short circuits. Fe RFBs, on the other hand, present a lower risk profile because of their aqueous solutions and the use of non-toxic iron-based electrolytes.

Fe RFBs are one of the key technologies for increasing the integration of renewable energy into the grid due to the abundance of Fe, environmental-friendliness, flexibility, and scalability.[85] The principle of a flow battery system consists of a power generation unit and an energy storage unit with ionic solutions used as electrolytes and stored in separate storage tanks. The electrolytes are circulated between the two units through flow channels and directed to the surface of the electrodes where the reaction takes place. The electrodes are inert and serve as catalyst supports. After the reaction is complete, the electrolytes are returned to the storage tanks where they are regenerated later during charging. Their efficiency was estimated to be around 70–80%, which is higher than fuel cells.[86] The electrochemical reactions of iron flow batteries were first proposed by Hruska and Savinell:[87]

$$\text{Positive electrode}: 2\text{Fe}^{3+} + 2\text{e}^- \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2\text{Fe}^+$$

$$E_{0+} = +0.77 \text{ V } vs. \text{ SHE}$$

$$\text{Negative electrode}: \text{Fe}^0 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \text{Fe}^{2+} + 2\text{e}^-$$

$$E_{0-} = -0.44 \text{ V } vs. \text{ SHE}$$

All-iron flow batteries utilize iron-based redox couples in the electrolyte solution. In this system, both electrolytes (anolyte and catholyte) are highly concentrated iron (ferrous and ferric) chloride aqueous solutions in two separate tanks, one with a reduced form of iron (Fe/Fe^{2+}) and the other with an oxidized form (Fe^{2+}/Fe^{3+}). Electrolytes are pumped into a cell stack separated by a selective anion exchange membrane. During charging, electrochemical redox reactions occur at both electrodes, converting electrical energy into chemical potential by changing the oxidation state of the iron ions. During discharge, the reactions reverse, releasing the stored energy as electrical power. The iron-based electrolytes offer advantages over other chemistry variants in terms of abundance, cost-effectiveness, and environmental safety. The energy storage capacity of an iron flow battery is determined by the total volume of electrolytes, while the power output is determined by the size and design of the cell stack.[88,89]

A comparative LCA study was conducted to evaluate iron-flow batteries and lithium-ion systems in industrial production the study revealed that the iron-flow batteries outperform lithium-ion systems in terms of selected materials and production parameters (*e.g.*, iron-based electrolytes and carbon-based cell stacks).[90] Additionally, the iron flow batteries offer several application advantages such as extended cycle life and the ability to independently manage power and energy operations. To further mitigate environmental impact, it is recommended to replace polymer resins with alternative materials that have lower ecotoxicity. In recent years, efforts have been made to develop a new generation of low-cost iron flow batteries for long-term energy storage systems, and among these, liquid flow batteries and hybrid flow batteries are interesting options.[91] A promising low-cost alkaline whole-iron flow battery was developed by coupling ferric/ferrous-gluconate complexes with $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system.[92] This new all-iron flow battery system exhibited a coulombic efficiency of over 99% and an energy efficiency of $\sim$83% at a current density of 80 mA cm^{-2} and can operate continuously for more than 950 cycles. Another potentially inexpensive approach to storing large amounts of energy is through the use of a redox concentration flow cell battery that uses aqueous iron chloride as a reacting solution on carbon electrodes.[93] This method is promising in terms of cycling and power density of the cell but still needs more work on cycling and chemical stabilization of the iron-based electrolytes, which could be achieved with the addition of organic acids like citric or ascorbic acid.

2.2.3. Iron batteries.

Iron batteries are solid-state devices where the electrodes and electrolytes have direct contact, yielding a fixed energy capacity determined by the battery's physical size. They are best suited for applications requiring a fixed capacity, such as residential power backups. However, they may encounter longevity challenges, such as dendrite growth.

Iron-batteries have a theoretical specific energy density of 1200 W h kg^{-1} which is way better than commercially available lithium-ion batteries (100–265 W h kg^{-1}).[94] They consist of a negative iron electrode, a positive air electrode, and an alkaline electrolyte. In this system, in the negative electrode half-cell, the iron oxidation from elementary through Fe(II) to Fe(III) occurs, while in the positive electrode half-cell, the reduction of oxygen occurs yielding iron oxides and resulting in a voltage of about 1.28 V.[95] The iron–air batteries are considered advanced secondary batteries due to the low solubility of the electrolytically deposited iron, which is a disadvantage for primary batteries. One example is an iron–air battery-microbial electrolysis cell system that was used to treat swine wastewater and produce hydrogen in a self-powered mode.[96] In this system, the iron–air battery produced coagulants necessary for pollutant removals such as carbon oxygen demand (COD) and electricity, while the microbial fuel cell powered by the iron–air battery generated hydrogen. Powered by a battery with an electrolyte concentration of 35 g L^{-1} NaCl, the COD removal rate of the microbial fuel cell with the coagulation process reached 98%, and hydrogen generation reached cca. 6 L per m^3 per day using raw swine wastewater and 57 L per m^3 per day using coagulated swine wastewater. The commercialization of Fe–air batteries is limited by certain drawbacks, including potential hydrogen leaks and anode passivation due to the formation of iron oxide films. These factors contribute to the low cycling stability of Fe–air batteries and lead to battery capacity deterioration.[97] Recently, among the various strategies to improve the efficiency of iron–air batteries, the use of ionic liquids (ILS) was proposed.[98] In this study, 1-ethyl-3-methylimidazolium L-(+)-lactate was used for the first time as an electrolyte additive to suppress hydrogen release and anode passivation for iron–air batteries. This method resulted in a capacity retention of more than 94% after 1000 cycles with a nominal capacity of 0.416 A h g^{-1} at a charging or discharging rate equivalent to one-fifth of the battery's capacity.

2.2.4. Emerging iron batteries

Rocking-chair iron-ion battery. Rocking-chair iron-ion batteries are new rechargeable aqueous metal-ion batteries without adverse electrolyte modifications that are more competitive than acidic all-Fe cells or zinc metal batteries, in terms of reactivity/dynamics, performance, and energy density.[99] In this system, Fe^{2+} ions circulate between an iron supplier anode and a host cathode. Wu *et al.* demonstrated the viability of Fe metals as anodes using a reversible Fe plating/stripping process in a $FeSO_4$ salt solution at a pH of $\sim$3–5 and reversible Fe^{2+} topotactic insertion into a Fe-based Prussian blue analog or $LiFePO_4$ cathodes at 1000 cycles.[36] Despite the advances, iron anodes are still plagued with side effects such as dissolution in acidic aqueous electrolytes, low coulombic efficiency (<80%), and sluggish redox reaction kinetics.[20]

Iron–hydrogen battery. Iron–hydrogen battery is a novel rechargeable aqueous battery system for large-scale energy storage,[100] designed as a static cell without using electrolyte pumping or circulation systems, which reduces manufacturing costs. It is based on the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple cathode and hydrogen gas anode in an alkaline solution. This battery operates at a current range of 10–60 mA, with an output voltage of 1.29 V, an energy efficiency of 93%, and an ultra-stable lifetime of over 20 000 cycles.

Battolyser. The battolyser combines two energy storage approaches electricity stored in a nickel–iron battery and as a water-splitting device that outputs hydrogen gas as the energy carrier.[101] The study conducted by Barton *et al.*,[102] showed that it can be used for both short- and long-term energy storage. The short-term is done by DC electricity storage as a Ni–Fe battery, while the long-term is through hydrogen gas, which evolves on the same Ni and Fe electrodes when the battery electricity storage capacity is fully charged or reached. In essence, the battolyser could serve as both an electrolyzer for power-to-X energy conversion and an electrochemical Ni–Fe battery.

3 Iron as circular fuel

In recent years, metal-fuel cycles have been proposed for large-scale thermal energy generation because their use avoids harmful emissions, is advantageous for storage and transportation, and has high energy density.[29] Aluminum, iron, magnesium, silicon, and titanium have been identified as feasible metal fuels that can be recycled and reused an unlimited number of times.[103]

Iron as a clean metal fuel is gaining importance. Still, a better understanding of the fundamental properties of iron combustion is required for the development of new iron fuel technologies. Detailed characteristics of iron combustion such as flame propagation,[104] flame temperatures of iron aerosols,[105] and the behavior of a single laser-ignited iron particle[106] have only recently become available.

A recent study conducted by Goroshin *et al.*[107] investigated the structure and velocity of laminar iron dust flames under controlled laboratory and microgravity conditions. The selected conditions eliminated factors such as particle sedimentation and bulk instability of dense dust clouds. Consequently, the study allowed observation of the flame at low velocities in suspensions containing large particles and slow-burning, non-volatile fuels. The study not only explored the potential applications of these findings in combustion systems but also shed light on the challenges and the promising prospects of solid fuels for propulsion and power generation purposes. To fully understand the implications of laminar flame experiments, it is crucial to combine the obtained results with numerical modeling and simulations that consider the underlying physics of the systems where these findings may find practical application. For this reason, various numerical models have been developed focusing either on the effect of slip, Stefan flow, evaporation, or the ignition phase.[108,109] More recently, the study by Thijs *et al.*[110] improved a 0D Lagrangian particle model for the first stage of diffusion-limited iron particle combustion (heat and mass transfer) using a boundary layer-resolved model.

The flame temperature of iron/air suspensions is 1500–1900 °C,[111] which is comparable to that of hydrocarbon fuels, but without CO_2 emissions. The solid iron oxides produced during combustion are easily recycled. Because of these fuel properties, the use of iron as metal fuel has been proposed for retrofitting coal-fired power plants.[112] Theoretically, replacing coal with iron in power plants could reduce CO_2 emissions by an estimated 10 million t per year.[113] A multi-stage feasibility assessment based on forecast data on iron, hydrogen, and renewable energy production, showed that a retrofit plan is feasible in reality. The proposed model combined existing technologies. Carbon-free carriers, such as iron, are used in a redox cycle. The oxidation of elementary iron by burning in oxygen releases heat and results in solid Fe_2O_3. The heat generates steam that drives the turbines which turn the generator as in a classic steam-compression cycle. There are no greenhouse gas emissions and the 'ash' in such a system are solid iron oxides that can be easily stored, transported, and recycled to elementary Fe and oxygen gas at the reduction facilities. Ideally, the iron oxides are reduced electrochemically using renewable sources or using green hydrogen for the thermochemical processes. This model is an example of a circular energy economy.[112] The phasing out of coal will need a long transition, predicted to be difficult for many countries. Some countries, such as Germany, plan to reach this goal by 2030.[114] Another example of here is the usage of iron powder as a circular fuel, which has been implemented in an industrial process in a beer brewing plant at Bavaria Brewery in Lieshout, near Eindhoven.[115]

3.1. Trends and challenges for sustainable iron production and recycling

The iron and steel industry, accounting for one-third of global CO_2 emissions, has received limited attention in terms of sustainable transition.[14,116] Despite the pressure to adopt more sustainable production methods, transitioning to low-carbon processes is a time-consuming and complex endeavor that involves radical innovations and thorough testing.[117,118] The industry is often seen as slow and resistant to large-scale transitions, but it is currently on the brink of a new technological shift driven by not only productivity and profitability but also the imperative of environmental sustainability. This urgency is primarily influenced by climate change mitigation policies aiming to reduce CO_2 emissions.[119] It was estimated that without taking appropriate measures, the emissions from industry could reach 2.7 Gt CO_2 per year by 2050, which is 7% higher than today.[120] To ensure a decarbonized energy future, it is essential to adopt planning technologies that prioritize reuse, redistribution, and remanufacturing, while placing significant emphasis on longevity and regenerative materials. In this context, the potential for sustainable iron production becomes a crucial topic of discussion. Specifically, we explore the possibilities of reducing iron using hydrogen as well as producing iron through electrolysis. By focusing on these approaches, we can pave the way forward toward a more sustainable and environmentally friendly iron production process.

3.2. Reduction of iron with hydrogen

To reduce the carbon footprint of the iron and steel industry, hydrogen metallurgy, namely the use of hydrogen as a reducing agent, is of great interest. Direct reduction of iron (DRI) in shaft furnaces or fluidized bed reactors,[121] hydrogen plasma-based reduction,[122] and direct injection of hydrogen into existing blast furnaces, in addition to coke[123] are three approaches considered to have high feasibility for future industrial applications. The direct reduction of iron with hydrogen, which adapts an already mature technology, is considered a promising method for achieving carbon neutrality in the iron and steel industry. This process was reported to be mainly carried out at high temperatures of 700–1000 °C, but also at lower temperatures (500 °C) for the production and separation of metallic iron from sandy and silty tailings.[124] Examples of projects that will commercialize large-scale hydrogen DRI plants in the future include the Hybrit project (already in operation) in Sweden with an expected increase in iron production of 1 million tons per year by 2025 (ref. 125) and projects by ThyssenKrupp ArcelorMittal planned for 2024 and 2030, respectively.

3.3. Hydrogen plasma iron reduction

Hydrogen plasma represents a promising carbon-neutral solution for iron production.[126–128] During hydrogen plasma reduction, a plasma arc zone forms between an electrode and the input iron ore (*e.g.*, hematite). In this zone, the ore is both melted and reduced by hydrogen, which exists in molecular and plasma states. The plasma state consists of ionized (H^+, H_2^+, and H_3^+), excited (H^*), and atomized (H) species formed through hydrogen particle collisions with electrons.[129] Hydrogen plasma reduction offers simultaneous ore reduction and melting, enabling the inclusion of scrap in the same process. However, hydrogen plasma reduction is still in the exploratory stage despite its thermodynamic efficiency. Souza Filho *et al.*[130] proposed a hybrid approach between hydrogen-based direct reduction and hydrogen plasma reduction to improve hydrogen and energy consumption of iron ore reduction. The results showed that this hybrid process consumes six times less hydrogen than laboratory-scale direct reduction at 700 °C. A hybrid approach allows the exploitation and maximization of specific technology characteristics and kinetically favorable regimes leading to reduced energy and hydrogen consumption, enhanced production stability, and an extended lifespan of the furnace. Moreover, it eliminates the need for unnecessary H_2 recirculation and enables cost-competitive production of pure iron.

The green hydrogen production required for iron ore reduction is expected to remain a challenge for the next two decades. Factors such as high recycling costs, inefficient conversion, energy-intensive production and storage of green hydrogen,[131] and the very high annual production demand of approximately 100 million tons[130] contribute to this challenge. However, studies have shown that CO_2 emissions in the iron and steel industry can be reduced by 78–95% if carbon is replaced by hydrogen from renewable sources.[132] Currently, the hydrogen supply side is still dominated by low-cost steam methane reforming and coal gasification. Water electrolysis powered with surplus hydro, wind, and photovoltaic power currently appears to be the only viable option to supply the required quantities of green hydrogen at an acceptable price.[133]

3.4. Iron production through electrolysis of iron oxide

Electrolysis is a promising solution for both iron recycling and production from iron oxide ore, due to minimal direct CO_2 emissions. However, the implementation of iron ore electrolysis has faced challenges such as low energy efficiency and the absence of a suitable anode material capable of withstanding high temperatures and corrosion.[134] Nevertheless, recent advancements in electrowinning[135] and molten oxide electrolysis[136] are prominent approaches in this field.

Electrowinning or electroextraction (a subset of electrolysis, specifically used to recover metals from aqueous solutions of their salts, the metal ions in solution are reduced at the cathode to form a metal deposit) is a promising technology that has already been demonstrated on a small scale.[135] In this process, the electrolyte is iron ore (iron oxide particles) suspended in an alkaline sodium hydroxide solution at an elevated temperature of 100–110 °C. The metallic iron is deposited on the cathode through the electro-reduction of iron(III) cations (Fe^{3+}), while the hydroxide anions are oxidized to oxygen gas at the anode. The obtained iron purity is high (∼99.98%), and the reported energy consumption is up to 3 kW h kg^{-1} Fe, for a setup with an iron production capacity of 5 kg per day.[137] Another example reported in the literature by Wang *et al.*[138] is the electro-reduction of Fe_2O_3 to produce metallic Fe at an even lower temperature of 110 °C in an alkaline solution.[138] In this study, an electrical-ionic conductive colloidal electrode containing electrochemically active Fe_2O_3 particles, NaOH solution, and a percolating electrical conductor (C-network) was applied.[138] The drawbacks currently preventing a practical application of low-temperature electrolysis include the issue of Fe_2O_3 particle adherence to the electrode surface, a low reaction rate, and low energy efficiency of Fe_2O_3 electro-reduction.[139]

Molten oxide electrolysis requires very high temperatures between 1550 and 1700 °C. Various electrolytes have been studied for this process, such as molten salts,[140] molten oxide, molten carbonates,[141] and a low-temperature approach by using aqueous solutions.[142] To make iron production more sustainable, reducing the working temperature of electrolysis has gained attention. In a study by Choi *et al.*,[143] the B_2O_3–Na_2O oxide system was shown to act as a supporting electrolyte for the electrochemical reduction of Fe_2O_3 to Fe at a lower temperature than any other molten oxide electrolysis method. In this case, the average energy consumption was 5.27 kW h kg^{-1} of Fe for electrolysis at 1000 °C which is low for an oxide melt. However, a challenge is ensuring a stable anode. Progress has been made in addressing the problem of anode oxidation by utilizing an electrically conductive solid solution of chromium and

Table 5 Comparison of CO_2 emission reduction potential and various characteristics from selected iron and steelmaking technologies (CO_2 emissions reduction are compared with traditional blast furnace–basic oxygen furnace (BF-BOF) ironmaking)

Production method	CO_2 emissions reduction potential	Advantages	Disadvantages/issues
DRI (coal-based)	38% (Ling *et al.* 2024 (ref. 155))	Large production; mature technology for industrial application	High-temperature operation (700–1000 °C); high hydrogen demand; cost of green hydrogen production; low iron oxide pellet quality
H_2DRI	6% (Ling *et al.*, 2024 (ref. 155))		
CH_4DRI	97% (Ling *et al.*, 2024 (ref. 155))		
DRI-EAF	Depends on the % of DRI used with scrap, 50% (35% scrap and 65% DRI) (Hornby and Brooks, 2021 (ref. 156))		
Hydrogen plasma smelting reduction	95% (Draxler, 2021 (ref. 157))	Thermodynamic efficiency; ability to include scrap in the process	Still in exploratory stage; high energy consumption; high temperature operation (1500–1700 °C)
Electrowinning	87–95%	High iron purity (up to 99.9%); low decomposition voltage, reduced oxygen evolution potential and minimal hydrogen evolution side reactions (Wang *et al.*, 2023 (ref. 158))	Low energy efficiency; anode materials; high operational temperatures (100–110 °C)
Molten oxide electrolysis	96% (Draxler *et al.*, 2021 (ref. 157))	Minimal direct CO_2 emissions; high iron purity (up to 99.9%)	Low energy efficiency; suitable anode materials; high operational temperatures (1550–1700 °C molten)
Deep eutectic solvent extraction	Depend on the lifecycle analysis, including DES component production and energy sources used (Zaib *et al.*, 2022 (ref. 159))	Low toxicity; biodegradability; cost-effective	Limited industrial scale application; need for optimization of solvents and processes

aluminum oxides with a corundum structure.[144] Another challenge is technological readiness, which currently is less than five on a scale of nine, and industrial development may not occur until 2045 or even 2050.[145]

Deep Eutectic Solvents (DESs) are formed by mixing two or more compounds at a certain molar ratio, where the melting point of the mixture is lower than that of each component. DESs exhibit great potential as functional electrolytes involved in electrochemical devices and energy storage systems, as well as for other various fields, due to their low toxicity, biodegradability, ability to dissolve a wide range of materials, environmental friendliness, and cost-effectiveness.[146–148] Moreover, their attractive features for ES technologies include low flammability, minimal volatility, high ionic conductivity, and excellent chemical stability. Several reviews have examined the utilization of DESs for metal extraction, recycling, and recovery.[149,150] Alongside their various applications, DESs also serve as flexible platforms for high-performance electrocatalysts, particularly for metal digestion and recovery, as metal oxides have significant solubility in DESs.[151] The literature on novel eutectics in electrochemistry focuses on binary eutectics of choline chloride and hydrogen-bond donors (*e.g.*, ethylene glycol, glycerol, oxalic acid, and urea).[152] Their extended applications are ternary or quaternary eutectics with a mixture of hydrogen-bond donors.[153] One example is calcium chloride hexahydrate eutectics with ethylene glycol, which provide a cheaper and more environmentally friendly liquid formation for metal recovery compared to other DESs. These have been successfully used in the electrodeposition of Fe, Co, and Ni at ambient temperature without additives.[154] In Table 5, selected iron and steelmaking technologies are summarized as environmentally friendly alternatives to the conventional blast furnace technology.

4 Conclusions

This paper highlights the transformative potential of iron in a decarbonized energy future, emphasizing its role as an energy carrier, particularly in the production of green hydrogen and grid energy storage. Innovations such as iron redox flow batteries (Fe RFBs) and iron–hydrogen batteries offer scalable, efficient, and non-toxic solutions for utility-scale storage. The battolyser system, which combines a nickel–iron battery with the production of hydrogen, is a versatile energy storage option. Iron-based chemical cycles, such as the $FeCl_2$ cycle for hydrogen production, and thermo–electrochemical cycles, where iron is oxidized with HCl acid, show the potential for sustainable closed-loop hydrogen production technologies. Innovative approaches such as hydrogen metallurgy and the electrolysis of iron oxide ore, promise to minimize CO_2 emissions and reduce the carbon footprint of iron and steel production. Despite challenges such as low energy efficiency and suitable anode materials, progress in electrowinning and molten oxide electrolysis is promising. Policy measures and technological advances are crucial for the uptake and recycling of iron-based technologies and emphasize the need for collaborative efforts to create a sustainable energy ecosystem.

Research into novel iron-based energy storage technologies that go beyond batteries, such as supercapacitors or hybrid systems that combine different storage mechanisms, also includes research into advanced materials and manufacturing processes to improve the performance and efficiency of these solutions. The integration of artificial intelligence and machine learning algorithms is crucial for optimizing the operation and management of iron-based energy storage systems. Interdisciplinary approaches for sustainable iron production and energy storage applications are utilized through collaboration with other industries and research areas. The focus is on the scalability and economic viability of iron-based technologies to facilitate their widespread adoption in the energy sector.

The future of iron-based energy technologies looks promising with advances in materials, production methods, and applications. Nanostructured iron materials offer higher efficiency, while hybrid systems combining iron batteries with supercapacitors offer high energy efficiency and fast-charging capability. Sustainable production methods, such as the integration of green hydrogen production with iron production, can significantly reduce CO_2 emissions. In addition, advanced electrochemical reduction techniques provide energy-efficient and environmentally friendly alternatives to conventional processes.

The transition to a circular economy concept further maximizes resource efficiency. By integrating sustainable practices into the entire life cycle of iron-based energy technologies, such as recycling and reusing materials, we can minimize waste and reduce environmental impact. LCA studies are critical to guiding sustainable practices by assessing the environmental impact of iron-based energy technologies, enabling informed decision-making, and promoting sustainable development.

Emerging applications of iron include its potential as a fuel or as a material for space exploration, as it is abundant and recyclable. The integration of iron-based energy storage into smart grids can improve grid stability and support renewable energy sources.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

Conceptualization: M. V. and A. O. M.; investigation: A. O. M. and U. L.; writing – original draft: A. O. M., U. L. and M. V.; writing – review & editing: A. O. M. and U. L.; visualization: U. L.; funding acquisition: M. V.

Conflicts of interest

There are no conflicts to declare.

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