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Photo-redox flow batteries as a promising pathway to sustainable energy storage: Case studies of Morocco and Poland

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Abstract: *Purpose*. The paper examines how photo-redox flow batteries can support a sustainable energy transition in Morocco and Poland by simultaneously harvesting and storing solar energy, thereby reducing dependence on fossil fuels and mitigating the intermittency of renewables. *Methodology*. The study combines a review of national energy policies and renewable energy targets with a comparative techno-economic assessment of photo-redox flow battery deployment scenarios in both countries, focusing on system performance, grid integration, and long-term sustainability indicators. *Results*. The findings show that photo-redox flow batteries can significantly increase the share of solar energy in national power mixes, improve grid stability, and lower lifecycle emissions compared to conventional storage and fossil-based generation, with particularly strong gains under high-renewables scenarios for Morocco and coal-replacement pathways for Poland. *Theoretical contribution*. The paper extends the emerging literature on next-generation energy storage by conceptualizing photo-redox flow batteries as a dual harvest–store technology and by linking their deployment to macro-level energy security, decarbonization, and resilience outcomes in middle-income and coal-dependent economies. *Practical implications*. The results provide policymakers and energy planners with evidence-

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based guidance on integrating photo-redox flow batteries into national energy strategies, including indicative design parameters, investment priorities, and regulatory measures to accelerate clean energy deployment while managing economic and geopolitical risks.

Keywords: Photo-Redox Flow Batteries (PRFBs), Morocco, Poland, renewable energy, energy storage, solar energy, sustainable energy storage

Sustainable Development Goals (SDGs): SDG 7: Affordable and Clean Energy; **SDG 9:** Industry, Innovation and Infrastructure; **SDG 13:** Climate Action

1. Introduction

The gradual expansion of global energy demand, driven by population growth, industrialization, transport electrification and the development of digital infrastructures is putting considerable pressure on nations to find more sustainable ways to produce and recover energy (Rezk et al., 2023; Zemlickienė et al., 2024; El Boutalbi et al., 2024; Amraouet al., 2024; Redouani et al., 2024; Talbi et al., 2025; Sebbaghi et al., 2025; Piccinetti et al., 2025; Taib et al., 2025; Rezk et al., 2025; Smaliukienė & Katina, 2025; Chiki et al., 2025; Vestertė et al., 2025). Global energy demand rose by around 2.2% in 2024, while electricity consumption jumped by around 4.3% over the same period, notably due to increased use in industry, cooling, and digital services. Traditionally, dependence on fossil fuels cannot meet this growing demand indefinitely without exacerbating climate change, pollution, and resource depletion. Countries are therefore turning to renewable energies such as solar, wind, and hydro power, which offer more environmentally friendly solutions to meet growing demand. Nevertheless, the intermittent nature of these renewable sources poses a significant challenge, without efficient energy recovery and storage systems to compensate for imbalances between supply and demand, much of the clean energy produced could remain unused or destabilize the power grid (Bethany, 2025).

In this context, photo-redox flow batteries (PRFBs) appear to be a promising technology for large-scale energy storage. Unlike conventional batteries, PRFBs integrate light capture directly into the redox flow system, enabling them to both capture solar energy and store it in liquid electrolytes. This dual functionality reduces the need for separate photovoltaic panels and recharging infrastructure, while improving energy conversion efficiency and sustainability (Chen et al., 2018). In addition, PRFBs easily adapt to grid requirements without compromising performance, enabling the direct conversion of solar energy into stored electrical energy. These devices offer a compelling solution to address the intermittency of renewable energy sources and support the transition to cleaner energy systems. Morocco, with its abundant solar potential, and Poland, facing the challenge of an energy transition in line with European decarbonization targets, could find PRFB solutions tailored to their national energy strategies. By examining the fundamental principles, recent advances, and potential applications of this emerging technology, this article highlights how PRFBs can help make global energy systems more resilient and sustainable.

2. Morocco

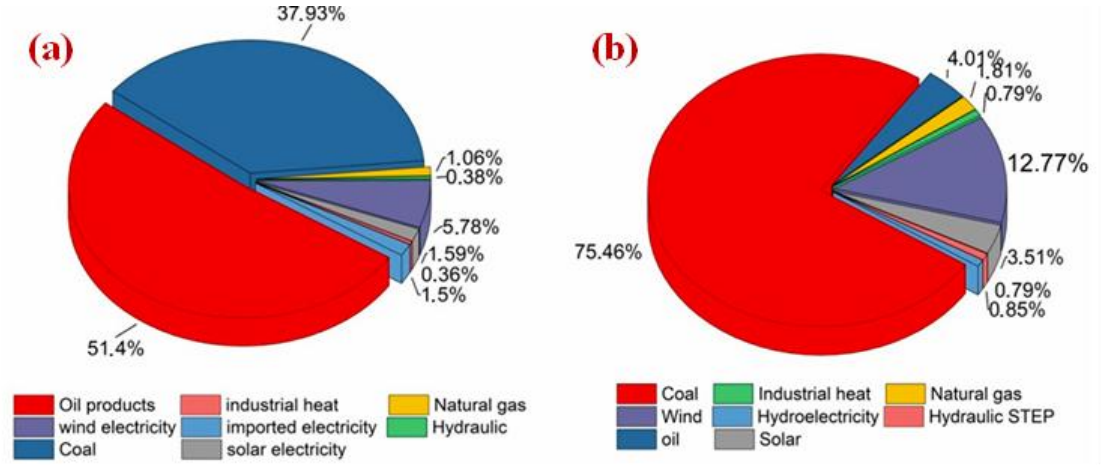
2.1. Morocco's historical energy composition

Morocco's energy sector has historically been heavily dependant on imported fossil fuels, particularly coal, oil, and natural gas, due to the scarcity of domestic hydrocarbon resources. Imports cover more than 90% of the country's energy needs, making Morocco one of the most energy-import-dependent countries in the MENA region. According to the national energy balance in Figure 1, oil accounts for approximately 51%, coal for 38% and renewable energies for just 8.8% of total primary energy supply (Benbba et al., 2024). This composition underscores Morocco's longstanding reliance on fossil fuels for electricity generation, particularly coal-fired power plants.

This heavy dependence has made Morocco vulnerable to global price volatility and substantial import costs, which negatively affect the national trade balance (Benbba et al., 2024). Beyond financial constraints, the energy portfolio, dominated by fossil fuels, is responsible for significant

greenhouse gas emissions, with the electricity sector accounting for approximately 45% of total CO_2 output (Benbba et al., 2024). Moreover, the rapid expansion of industrial and residential electricity demand, which is expected to increase by around 5% annually since 2004, has exacerbated these issues (Sakhraoui et al., 2024).

Figure 1: Breakdown of primary energy demand in 2022 (a), Overall energy consumption in Morocco during 2022 (b)



Source: Bennouna, 2023

The geopolitical risks associated with fossil-fuel imports were clearly illustrated by the closure of the Maghreb-Europe gas pipeline in 2021, which interrupted natural gas deliveries and forced Morocco to turn to more expensive liquefied natural gas imports (Benbba et al., 2024). As a result, the current energy mix raises pressing concerns regarding energy security, economic fragility, and environmental sustainability. These limitations have prompted Morocco to reassess its energy strategy and accelerate the transition to renewable sources (El Hafdaoui et al., 2025a; Laaroussi & Bouayad, 2020).

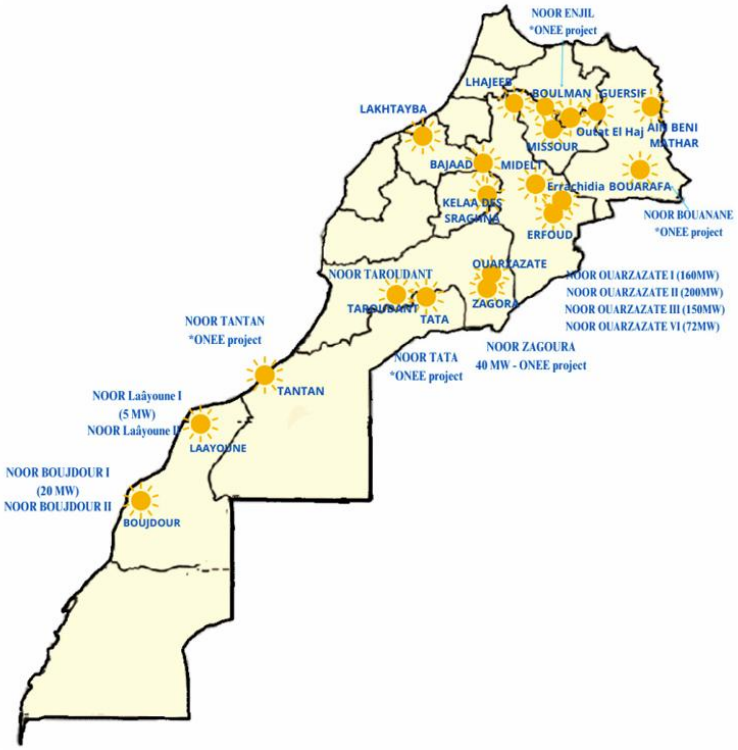
2.2. Morocco's strategy for energy transition and the central role of solar energy

Faced with growing energy needs and its dependence on fossil fuel imports, Morocco adopted a comprehensive national energy strategy in 2009 aimed at reshaping its electricity sector to ensure its sustainability. This strategy is based on four pillars: energy security through diversified supply, affordable access, environmental protection through renewable energy, and regional cooperation. This plan established key institutions, such as MASEN (2010), ONEE, and AMEE, to manage renewable energy initiatives and regulations (Benbba et al., 2024). The targets include an installed renewable energy capacity of 42% by 2020, 52% by 2030, and 70% by 2040, in line with the Paris Agreement goals (Amegroud, 2015.)

Solar energy is driving this change, exploiting Morocco's primary resources: an average GHI of 5.8 kWh m^{-2}. day^{-1} and DNI of 1800–3000 kWh m^{-2}. $Year^{-1}$ in areas like Ouarzazate and Errachidi (Benbba et al., 2024). The Noor program (Figure 2) illustrates this with the Ouarzazate complex between 2016 and 2018, providing 580 MW of energy from Concentrated Solar Power (CSP) and solar Photovoltaic (PV), thereby reducing CO_2 emissions by 760,000 tons per year. Expansion projects include Noor Midelt (800 MW hybrid) and decentralized PV initiatives such as Noor Atlas. Supporting measures encompass PROMOSOL and SHEMSI for solar water heating, as well as more than 10.000 PV irrigation pumps to reduce fuel consumption in rural areas (El Hafdaoui et al., 2025b). The Green Hydrogen Strategy targets 8 GW of new renewable energy by 2030, using solar electrolysis to produce clean fuels.

Challenges remain, including concentrated solar power (CSP) costs, limited local PV production, grid inflexibility, storage needs, regulatory barriers, and financing gaps (Amegroud, n.d.). Solutions include supporting local industry, advancing storage technologies such as photo-redox flow batteries, and improving connections to the European grid. In 2023, renewables exceeded 41% of capacity, proving that emerging markets can drive transformation through policy, institutions, and vision.

Figure 2: Geographic distribution of major solar power projects in Morocco, including the NOOR and ONEE initiatives



Source: Masen, 2020

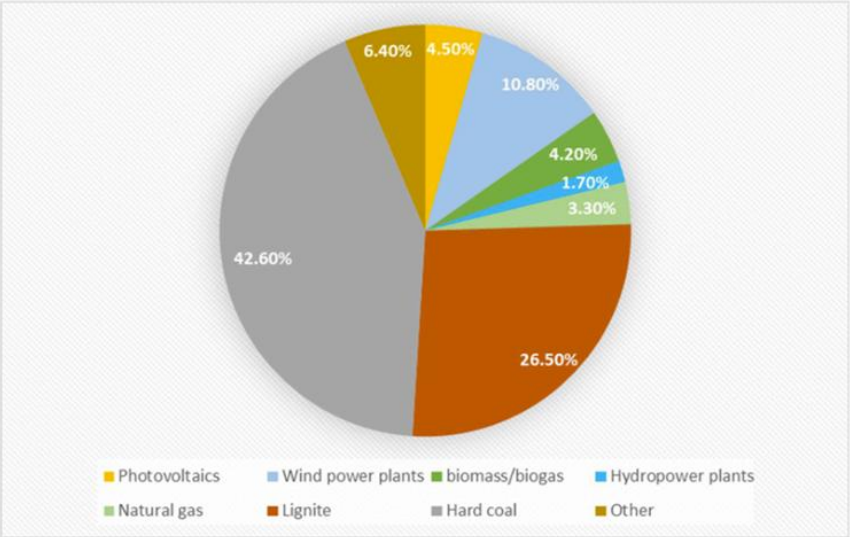
3. Poland

3.1. Historical energy mix of Poland

The Polish energy sector has long been dominated by coal and lignite, highlighting its heavy dependence on local fossil fuels. Under Soviet rule, particularly from the 1970s to the 1990s, the country built a highly carbon-intensive energy infrastructure, resulting in extensive environmental damage and inefficient consumption patterns. This period was characterized by high energy intensity, minimal hydrocarbon utilization, and a pricing mechanism that encouraged wastefulness by decoupling energy costs from economic logic. Coal has played a pivotal role in safeguarding Poland's energy security and, despite its declining dominance, remains a key component of the energy mix. Over the years, repeated attempts to restructure the coal mining sector have fallen short of expectations (Kotelska, 2025) primarily due to the entrenched perception of coal's vital importance to national security, as well as the influential power of mining unions, whose views have historically been and continue to be taken into account by every Polish government. Coal-fired power plants were the core of the electricity grid, a configuration that persisted into the 2000s with scant modernization. Despite joining the EU in 2004, coal remained the dominant fuel, comprising 42.6% of electricity production in 2020 (Figure 3) and positioning Poland among the most coal-reliant nations in Europe.

Faced with growing economic, environmental, political, and legal pressures, especially from the European Union, Poland began a concrete shift away from coal around 2019, as the sustainability of its carbon-intensive energy model came under intense scrutiny. Economically, rising extraction costs, depleting reserves, and the rising viability of imported fuels and renewables have eroded coal's dominance in electricity generation. Environmentally, growing concerns about air pollution, CO_2 emissions estimated to be 316.41 (Kt.) in 2020 (Mrozowska et al., 2021), and health impacts have accelerated the fight against the use of fossil fuels. Politically and legally, European Union instruments such as the Emissions Trading System and the European Green Deal have imposed penalties for exceeding emissions. In 2018, with coal still accounting for 73.6% of electricity production, its lack of economic viability became apparent, prompting reforms in favor of renewable energies (Zupančič et al., 2018).

Figure 3: Poland's electricity generation breakdown (%) in 2022



Source: Czepło & Borowski, 2024

3.2. Poland's strategy for energy transition and the central role of solar energy

Poland's energy transition strategy, as detailed in the Polish Energy Policy until 2040 (PEP2040), prioritizes a phased exit from coal dependence in favor of diversified, low-carbon alternatives, positioning solar energy as a cornerstone of this shift. This plan targets slashing coal's share of electricity from over 70% to less than 11% by 2040, in line with EU climate mandates and national sustainable development goals. Solar PV has gained prominence for its scalability, speed of installation, and lower costs, making it suitable for decentralized and prosumer models.

Initiatives such as the (My Electricity) (Mój Prąd) program and net metering have accelerated its adoption, particularly in households, propelling Poland to become one of the fastest-growing solar sectors in Central Europe. Although solar resources are modest compared to those in southern Europe, they are sufficient for large-scale deployment, especially in rural areas and former mining regions undergoing ecological revitalization. By emphasizing decentralized solar energy alongside grid upgrades and EU funding, the strategy highlights its contributions to energy autonomy, technological progress, and regional economic renewal, thereby consolidating solar energy's role as a catalyst for a resilient, diversified, and sustainable energy landscape (Dębicka et al., 2024).

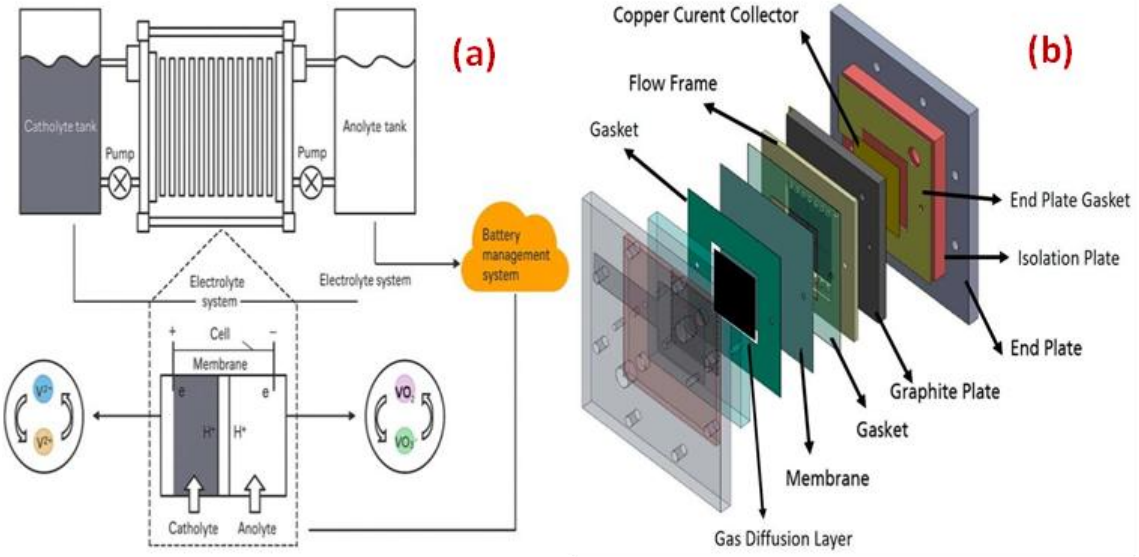
4. Basics of redox flow batteries (RFBs)

4.1. Components and working principle

Over the past few decades, electrochemical energy storage (EES) devices have emerged as key technologies for large-scale integration of renewable energy into the power grid (Luo et al., 2015). Redox flow batteries (RFBs) are electrochemical energy storage devices that store energy in liquid electrolytes containing redox-active species. Unlike conventional solid-state batteries, in which energy is confined to the electrodes, RFBs separate power and energy (Z. Huang, Xiao, et al., 2025). This system is built around three key components (Figure 4.a): the cell, the electrolytic system, and the battery management system. These components work in synergy to ensure efficient energy storage and release. The cell is the central component of RFBs, where the electrochemical reactions that enable the mutual conversion between electrical and chemical energy occur.

Charging and discharging cycles are achieved by electron transfer in the external circuit and by ion migration in the electrolyte. Typically, a battery comprises several individual cells connected in series or parallel. The structural components of a single cell include the ion exchange membrane, which separates positive and negative electrolytes while facilitating ion conduction, as well as electrodes, electrode frames, seals, bipolar plates, current collectors, insulating plates, connecting plates, and nuts (Figure 4.b). Among these elements, electrodes often use porous carbon-based materials that provide the reaction interface and catalyze the redox reactions of the active substances (Jiang et al., 2023; Y. Liu et al., 2025; Loghavi & Zarei-Jelyani, 2023).

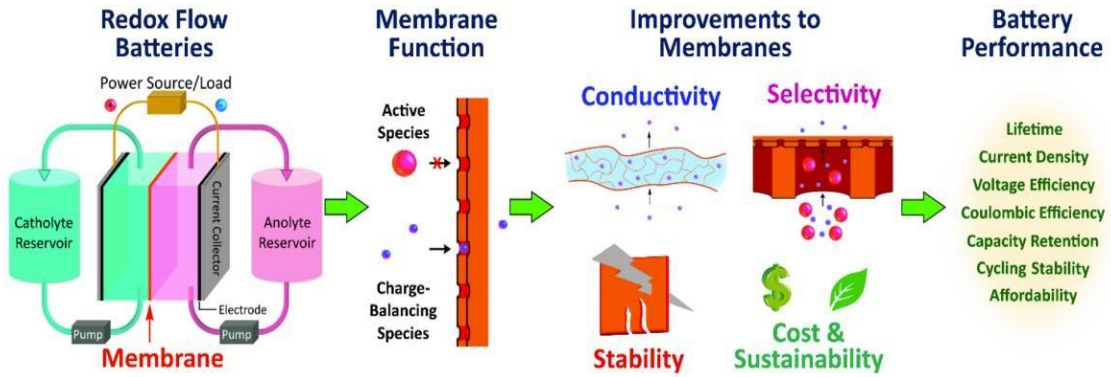
Figure 4: Schematic representation of a redox flow battery, operating principle with electrolyte circulation and redox reactions (a), 3D view of the cell components (b)



The proton exchange membrane (PEM) is another key component of the RFB. It regulates the transport of ions between the two half-cells while ensuring the chemical separation of the electrolytes (Figure 5). Its primary function is to allow H^+ protons to pass between the two electrolyte compartments, maintaining charge balance during redox reactions at the electrodes. At the same time, it prevents the passage of active redox species between the anolyte and catholyte solutions, which would lead to contamination, capacity loss, and self-discharge (Leba Akman et al., 2025).

The electrolytic system mainly comprises electrolyte storage tanks, pumps, and piping. It is one of the most essential components of a deep-cycle battery (RFB), as its energy storage capacity and electrochemical performance are directly linked to it. In a conventional RFB, two electrolytes, commonly referred to as catholyte and anolyte, are stored in separate tanks and circulate through the electrochemical cell during operation. These solutions contain redox-active species that undergo reversible oxidation and reduction reactions at the electrodes, enabling conversion between electrical and chemical energy (Leba Akman et al., 2025). Consider the example of vanadium RFB, whose tanks store V3+/V2+ and V5+/V4+ solutions, a common choice for commercial purposes for years (Ulaganathan et al., 2016; Voropay et al., 2024). This popularity stems from the fact that the transfer of redox-active species between half-cells does not permanently reduce cell capacity, as vanadium ions can return to their initial oxidation state during recharging.

Figure 5: Role and impact of the proton-exchange membrane in redox flow batteries



Source: (Machado et al., 2021)

During charging, electrical energy is applied to the cell, causing vanadium ions to be oxidized from a lower to a higher oxidation state. On the positive side, V^{4+} (VO^{2+}) is oxidized to V^{5+} (VO_2^+), while on the negative side, V^{3+} is reduced to V^{2+}. This process is facilitated by ion exchange across the membrane, which selectively allows H^+ ions to pass, thereby maintaining charge neutrality throughout the system. Conversely, during discharge, the chemical reactions are reversed: VO2+ is

reduced back to VO2+, and V2+ is oxidized to V3+, releasing the stored energy as electrical energy (Cheng et al., 2025; Guarnieri et al., 2025a; Marahatta, 2025; Zou & Jung, 2025). The following equations (1,2,3,4,5, and 6) describe the reactions taking place at the electrodes (Bandpey et al., 2025; Guang et al., 2025, 2025) :

$$VO_2^+ + 2H^+ + e^- \longleftrightarrow VO^{2+} + H_2O \qquad E^0 = 1.004\,V/SHE \qquad (1)$$

$$V^{3+} + e^- \longleftrightarrow V^{2+} \qquad E^0 = -0.255V/SHE \qquad (2)$$

- *Charge direction*

Anode

$$V^{2+} \rightarrow V^{3+} + e^- \qquad (3)$$

Cathode

$$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O \qquad (4)$$

- *Discharge direction*

Anode

$$V^{3+} + e^- \rightarrow V^{2+} \qquad (5)$$

Cathode

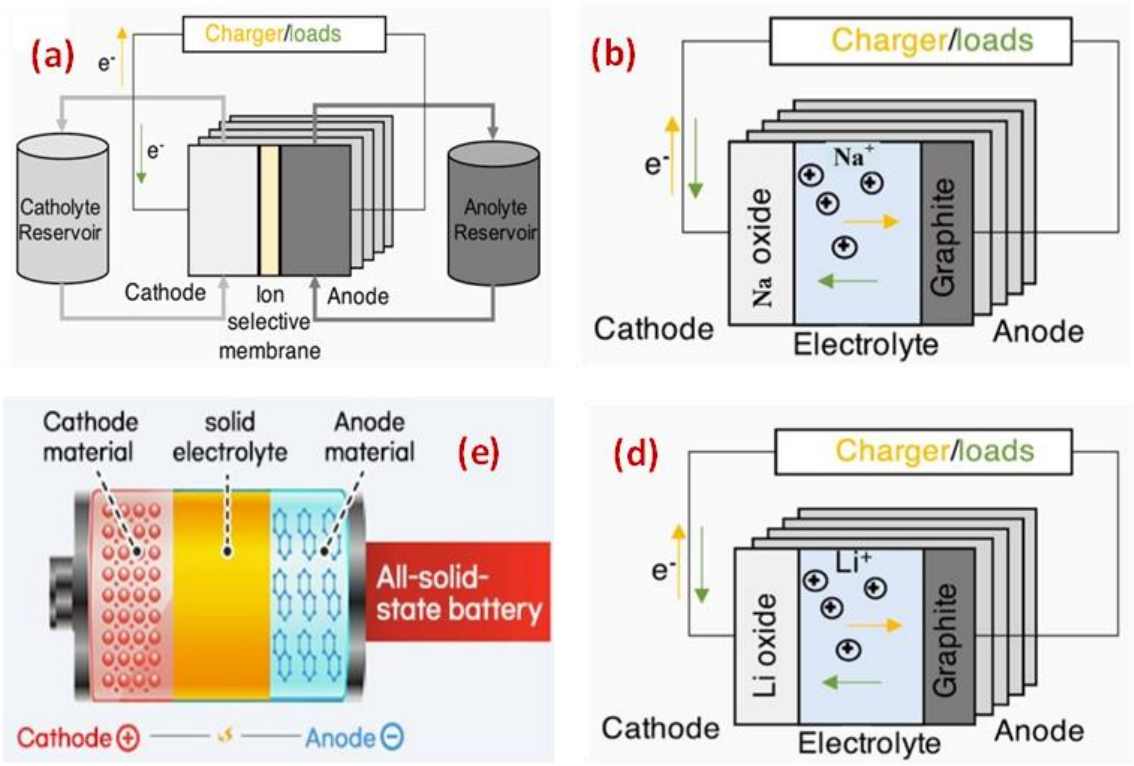
$$VO^{2+} + H_2O \rightarrow 2H^+ + e^- + VO_2^+ \qquad (6)$$

4.2. RFBs vs Lithium-ion, Sodium-ion and Solid-State Batteries

4.2.1. Chemistry and charge storage mechanisms

As shown in Figure 6, RFBs store energy in liquid solutions containing redox-active chemicals. These liquids are pumped through electrochemical cells when the battery is in use, allowing the amount of stored energy and the power delivered to be controlled independently. On the other hand, traditional Lithium-ion (Li-ion) and Sodium-ion (Na-ion) batteries work quite differently. They are closed systems in which ions move in and out of solid electrode materials, such as lithium cobalt oxide ($LiCoO_2$) or sodium iron phosphate ($NaFePO_4$) (Abraham, 2020; Wenhua et al., n.d.). In these batteries, energy capacity and power output are closely linked as both depend on the properties of the solid electrodes. Solid-state batteries (SSBs) take a different approach by replacing the liquid electrolyte with a solid ionic conductor (Lou et al., 2021). This design can support higher voltages and improve safety, but it also introduces challenges, such as interface resistance and more complex manufacturing processes. Thus, while RFBs rely on redox reactions in fluid electrolytes, Li-ion and SSBs depend on the ion intercalation into solid lattices, leading to fundamentally different performance characteristics.

Figure 6: Comparative schematic illustrating the chemistry and design of various battery types, including redox flow, sodium-ion, lithium-ion, and all-solid-state batteries including, RFBs (a), Na-ion (b), solid-state battery (c) and Li-ion (d)



Source: Dang et al., 2024; Naseer et al., 2025

4.2.2. Energy storage technologies

Energy efficiency is a key metric for evaluating an energy storage system, indicating how much of the stored energy can be used without waste. Alongside this, the system's rated power and capacity are two essential specifications: rated power indicates the maximum power output during discharge, while capacity tells you the total amount of energy it can hold, and both directly influence how the system fits into real-world applications. For a fixed rated power, the discharge duration, essentially how long the system can keep delivering that power, reveals the scale of its energy capacity. The duration and rated power of various ESTs are shown in Table 1. Beyond specification factors like safety, the availability of the resources needed for construction, and environmental footprint, economic feasibility also plays a significant role in shaping the future of ESTs. Table 1 provides a side-by-side comparison of different electrochemical EST across all these aspects, providing a clear and complete view of their unique characteristics and overall potential for growth and adoption.

Table 1: Comparative summary of key performance parameters and characteristics of different

Energy storages	Battery type			
	RFB	Li-ion	Na-ion	Solid-state
Resource abundance	Medium	Low	High	Low
Environmental impact	High	Medium	High	Low
Safety	High	Medium	High	High
Lifetime (cycles)	12000 to 18000	1000 to 5000	2000 to 4000	5000 to 10000
Power rating (MW)	1 to 200	0 to 100	0 to 50	0.3 to 1.2
Energy density (Wh/kg)	10 to 35	75 to 200	50 to 150	250 to 400
Duration (hours)	0 to 4	0 to 4	0 to 4	1 to 5

Source: Famprikis et al., 2019; Li et al., 2018; Mahlia et al., 2014; Rad et al., 2020; Schöne et al., 2022; Wali et al., 2024; Zhang et al., 2018; Zhao et al., 2020

4.3. Limitations of RFBs

4.3.1. Low energy density

A key drawback of Redox Flow Batteries is their relatively low energy density, which is comparable to that of Li-ion batteries or even solid-state batteries. This issue stems mainly from the limited solubility of redox-active materials in the electrolyte and the modest cell voltage (1.26 V) in standard configurations such as VRFBs (Q. Huang et al., 2025). Researchers are working on improvements, such as incorporating mixed-acid electrolytes, non-aqueous solvents, or organic redox pairs, that could increase energy density. However, these approaches often entail trade-offs, such as higher viscosity, reduced chemical stability, and heightened safety risks (Yu & Manthiram, 2022).

4.3.2. Ion crossover and electrolyte imbalance

One ongoing challenge for RFBs is the crossover of ions through the selective membrane, leading to electrolyte imbalance, gradual capacity loss, and reduced efficiency over extended use. In VRFBs, for instance, V^{2+} and V^{5+} ions may migrate across the membrane, mixing into the wrong compartments and upsetting the redox balance (Kyeongmin et al., 2019). Even with advancements in materials like Nafion and hydrocarbon-based membranes, it's tough to strike the perfect balance among high ionic conductivity, long-term chemical stability, and adequate selectivity for vanadium ions. This ion crossover not only erodes the battery's capacity but also triggers pH changes and unwanted electrolyte precipitation, requiring regular rebalancing and maintenance. While innovative solutions such as specialized membrane coatings and optimized flow designs are emerging, they tend to add layers of complexity and raise overall costs (W.-F. Liu et al., 2023).

4.3.3. Kinetic limits and efficiency losses

RFBs frequently face slow redox reaction kinetics on electrode surfaces, resulting in lower voltage efficiency, typically 70 to 85% compared to Li-ion batteries, which exceed 90%. The reaction speeds for vanadium-based couples, especially the V^{3+}/V^{2+} pair, are hindered by electron transfer barriers and limitations in mass transport (Pan et al., 2026). Additionally, during charging, hydrogen evolution reactions (HER) can occur at the negative electrode, depleting active materials and worsening overall performance (Guarnieri et al., 2025b). Applying catalytic enhancements to graphite felt electrodes, such as the incorporation of dopants like cobalt or nickel, has improved kinetics. These modifications often introduce greater complexity and higher costs. As a result, refining electrode architecture, surface properties, and flow field configurations continues to be a critical focus for research aimed at minimizing these kinetic drawbacks.

4.3.4. Electrolyte instability and thermal sensitivity

Another key constraint in RFBs is the chemical instability of the electrolyte, especially the vanadium species in sulfuric acid environments. With prolonged operation or temperature variations, V^{5+} tends to form precipitates like V_2O_5, which lowers the concentration of usable vanadium and diminishes the overall capacity of the system (Zou & Jung, 2025). To mitigate this degradation, the electrolyte must be kept within a tight temperature range of 10 to 40°C, which increases the energy demands for cooling or heating systems. Moreover, undesirable side reactions, such as oxygen evolution and electrolyte breakdown at high charge levels, further restrict the battery's usable range. Emerging solutions like mixed-acid blends and stabilizing additives have enhanced solubility, yet they often lead to higher viscosity and increased corrosion risks (Naseer et al., 2025).

4.3.5. System integration and operational complexity

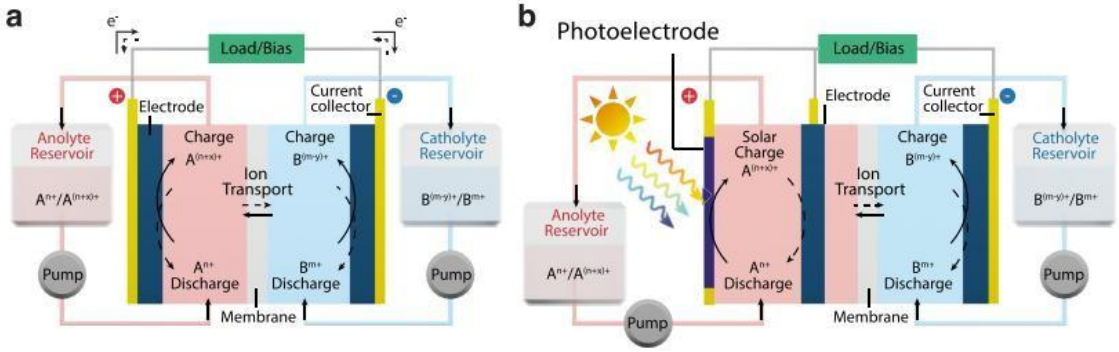
RFBs require careful oversight of fluid dynamics, temperature control and electrolyte equilibrium resulting in more intricate system management than solid-state alternatives. Factors like pump energy use, pressure drops and flow field design have a direct impact on overall performance and efficiency (Z. Huang, Liu, et al., 2025). During extended operation, issues such as shunt currents, corrosion and component fatigue can arise requiring regular maintenance to keep things running smoothly. Furthermore, incorporating RFBs into fluctuating renewable energy configurations

requires sophisticated monitoring and predictive algorithms to sustain electrolyte balance and refine charging processes. These refined hurdles position RFBs as a better fit for fixed, controlled grid-scale applications rather than portable or mobile uses.

5. Photo-Redox Flow Batteries (PRFBs) concept

Many researchers view Photo-Redox Flow Batteries (PRFBs) as a specialized variant of traditional RFBs, as most PRFB prototypes borrow directly from RFB designs, including their device architectures and redox-active pairs. PRFBs also benefit from this advantage, as they share the same decoupled power/energy device architecture with traditional RFBs (Figure 7) (Park et al., 2016; Raihan & Dyker, 2025; Xiaoliang & Wenxiao, 2017). For both, developing suitable redox couples remains a substantial scientific challenge. The redox-active species dissolved in the anolyte and catholyte not only directly govern the cell potential and energy density of PRFBs but also play a crucial role in influencing the performance and stability of the photoelectrodes (Pv et al., 2010; Ulaganathan et al., 2016).

Figure 7: Schematic comparison between RFBs (a), PRFBs integrating a photoelectrode for direct solar charging (b)



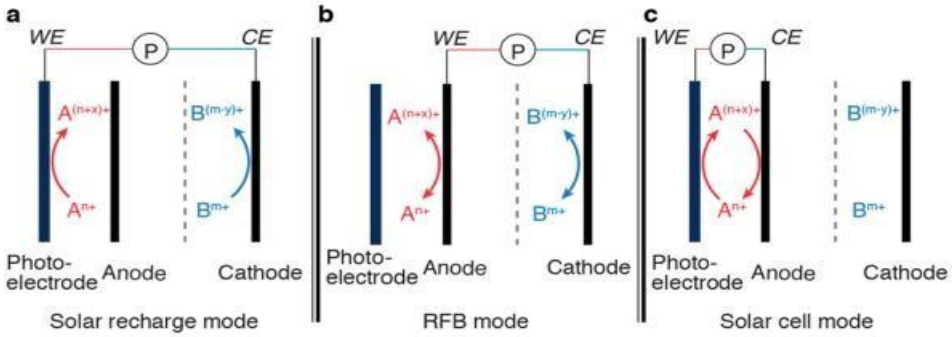
Source: Wenjie & Song, 2020

5.1. Working principle

As shown in Figure 8, the two systems have striking structural similarities, including two chambers divided by a membrane containing liquid electrolytes and reversible redox couples. This inherent similarity facilitates the merging of these systems into a single unified PRFB. As depicted in Figure 8, a standard integrated PRFBs design incorporates three electrodes: a photoelectrode, an inert cathode, and an inert anode. In operation, the semiconductor photoelectrode captures solar energy and generates photoexcited carriers that accumulate at the semiconductor liquid electrolyte interface to charge the redox couples of the electrolytes, thereby efficiently storing solar energy within them. This charging mechanism mirrors the process of photoelectrosynthetic cells. Depending on the photoelectrode configuration, PRFBs may utilize either two photoelectrodes for dual-sided illumination or a single photoelectrode.

When electrical power is required, the charged redox couples are discharged at the inert electrode, as in a conventional RFB, thereby producing electricity. Additionally, this device can function as a pure solar cell by continuously circulating the redox couples between the photoelectrode and the inert counter electrode within the same chamber; it thus produces electricity directly without any intermediate storage in a process similar to that of regenerative photoelectrochemical solar cells. Through these versatile modes, PRFBs are equipped to fulfill all essential roles in independent solar energy systems, eliminating the need for external electrical input.

Figure 8: Operating modes of PRFBs: solar recharge mode (a), conventional RFB (b) and solar cell mode (c)

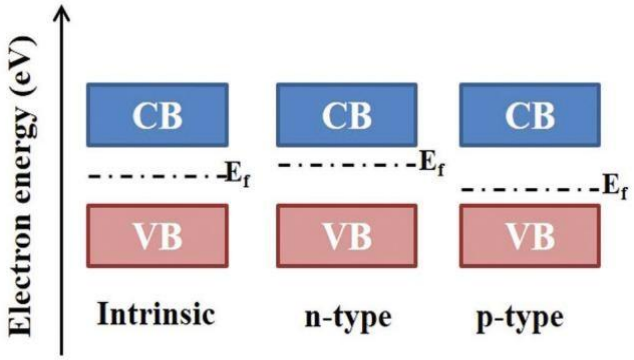


Source: Wenjie & Song, 2020

5.2. Semiconductor

Semiconductors play a pivotal role in PRFBs as the core component of photoelectrodes that convert light into chemical energy. Designing high-performance PRFBs requires a thorough understanding of the core physics underlying semiconductor devices, the thermodynamics governing semiconductor-liquid interfaces, and the operational mechanisms of photoelectrochemical cells. In inorganic semiconductors, electron energy levels are separated by a forbidden energy gap, or bandgap, which gives rise to an occupied valence band (VB), the highest filled frontier band, and an unoccupied conduction band (CB), the lowest empty band. The bandgap energy (E_g) is defined as the energy difference between the bottom of CB and the top of VB. The Fermi level (E_f) represents the electron energy for which the occupation probability is 50% at absolute zero temperature (0°K). In an intrinsic semiconductor where the electron concentration equals the hole concentration, the E_f is positioned approximately at the midpoint of the bandgap. In semiconductors doped with donor atoms (n-type doping), the Fermi level (E_f) shifts toward the CB, whereas in those with acceptor atoms (p-type doping), it moves closer to the VB (Rajeshwar, 2007). Figure 9 illustrates the band diagrams and the relative positions of E_f. When the energy of incident light (hν) exceeds the semiconductor's bandgap energy (E_g), electron-hole pairs are generated with electrons being excited and promoted to the CB and holes remaining in the VB.

Figure 9: Energy band diagram of semiconductors: comparison between intrinsic, n-type, and p-type materials



Source: Cao et al., 2018

5.2.1. Semiconductor-liquid junction

It is important to distinguish between the reference scales used to describe semiconductor energy levels. In solid-state physics, electron energy is typically referenced to the vacuum level, whereas in photoelectrochemistry it is commonly expressed relative to the standard hydrogen electrode (SHE) scale. The conversion between these electron energy levels can be calculated using equation (7) (Allen & Martin, 2007):

$$E_{e(vac)} = -4.5 - eE_{e(SHE)} \quad (7)$$

Here, $E_{e(vac)}$ denotes the electron energy level relative to the vacuum scale (in eV) in the semiconductor, while $E_{e(SHE)}$ represents the potential (in V) referenced to the standard hydrogen electrode (SHE).

When a semiconductor is immersed in a solution, the potential difference drives the system toward electronic equilibrium, resulting in three key effects:

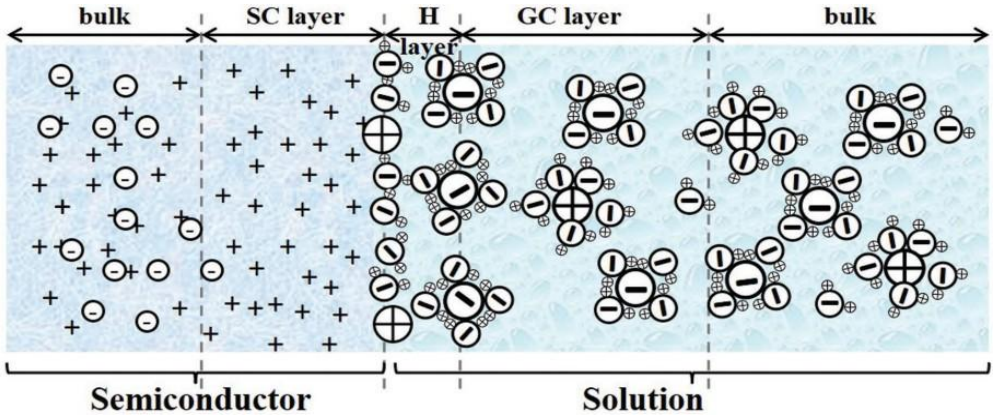
i. Equal charge distribution on both sides due to the alignment of energy levels between the semiconductor and the solution. This condition defines the flat band potential.

ii. Accumulation of electrons at the semiconductor's surface, forming an accumulation layer.

iii. Migration of electrons into the solution, creating a depletion layer on the semiconductor side.

The accumulation or depletion layer on a semiconductor is collectively known as the space-charge (SC) layer. On the electrolyte side, a Helmholtz (H) layer and a Gouy-Chapman (G) layer (Grätzel, 2001) are formed as illustrated in Figure 10.

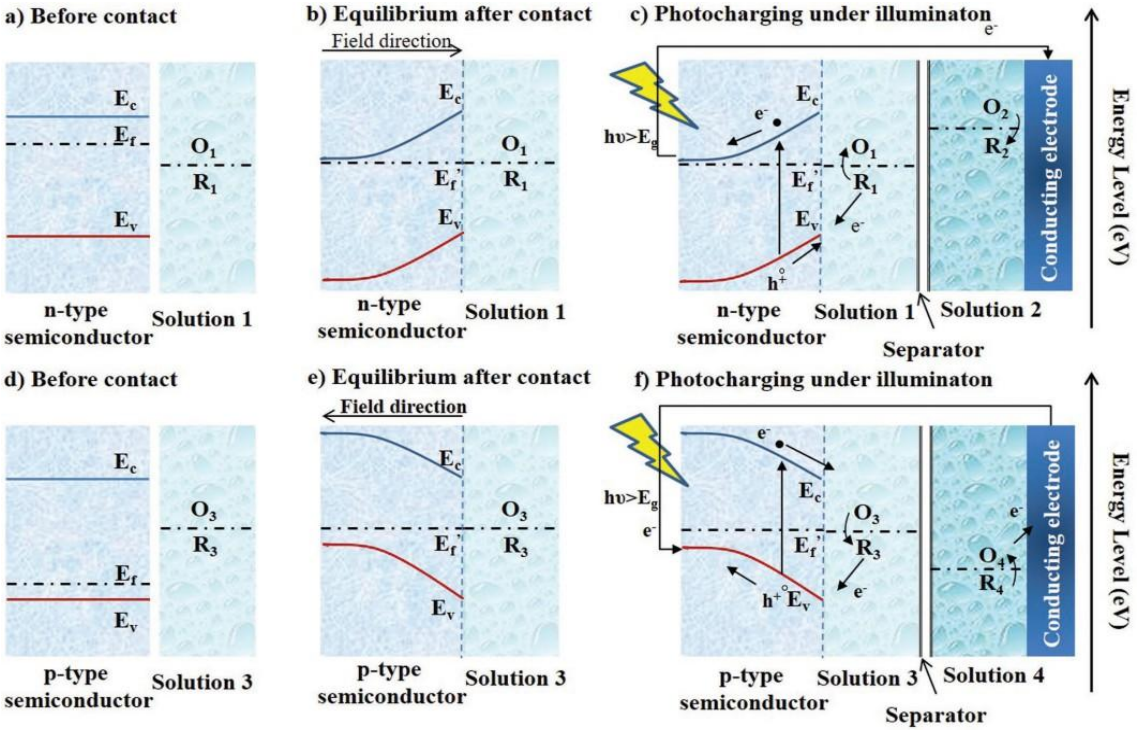
Figure 10: Schematic illustration of the semiconductor–electrolyte interface showing charge distribution across the space charge (SC), Helmholtz (H), and Gouy–Chapman (GC) layers



The space-charge (SC) layer is essential for photocharging, which converts photon energy into chemical energy. As shown in Figure 10, for an n-type semiconductor whose Fermi level (E_f) exceeds the redox potential of the redox electrolyte, electrons flow from the CB to the redox molecules in solution, establishing an electric field directed from the semiconductor bulk toward its surface. Upon illumination with light of energy $h\nu > E_g$, electron-hole pairs are generated and subsequently separated by the electric field, which leads to migration of electrons toward the bulk (Downhill movement) while holes move to the surface (Uphill movement).

If the redox couple O_1/R_1 in the solution has a higher redox energy level than that of photogenerated holes, the oxidation of R_1 can occur. Concurrently, if the semiconductor is connected to a counter electrode immersed in another solution containing O_2/R_2 and separated by a membrane (Figure 11.c), the photogenerated electrons can be transferred to the conduction band (CB) migrate to the surface of the counter electrode and reduce O_2 at the solution/electrode interface provided that the redox energy level of O_2/ R_2 is lower than that of the electrons. A similar process applies to a p-type semiconductor immersed in a solution with O_3/R_3 and having appropriate redox energies; the electric field directs from the surface toward the bulk (Figure 11.d). Under illumination, the holes migrate to the bulk while the electrons move back to the surface, enabling the reduction of O_3 in the solution if the energy levels align (Figure 11.e). When connected to another electrode in the O_4/R_4 solutions where its redox energy level lies between that of O_3/R_3 and the valence band energy (E_v) of the p-type semiconductor, the oxidation of R_4 occurs at this electrode's surface (Figure 11.f) (Allen & Martin, 2007; Bard, 1979). In summary, sufficiently energetic light facilitates photo-oxidation at the surface of an n-type semiconductor and photoreduction at the surface of a p-type semiconductor.

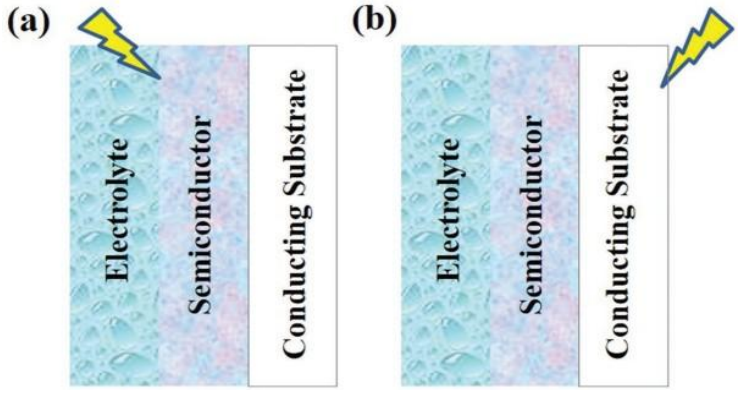
Figure 11: Energy band diagrams illustrating charge transfer processes at n-type and p-type semiconductor–electrolyte interfaces, n-type (a, b, and c), p-type (d, e, and f) configurations before contact, after equilibrium, and under illumination



5.3. Photoelectrode

The formation of a space-charge layer at the semiconductor/electrolyte interface under illumination provides the driving force for photocharging the battery. The relative positions of the light source, photoelectrode, and electrolyte significantly influence light absorption efficiency and must not be overlooked. Depending on the setup, the photoflux reaching the semiconductor may be attenuated by either the electrolyte or the substrate corresponding to front-side and back-side illumination modes, as depicted in Figure 12.

Figure 12: Illumination configurations for photoelectrodes, front-side illumination through the electrolyte (a) and back-side illumination through the conducting substrate (b)



Beyond light absorption by the surrounding media, the illumination mode also influences the diffusion length of charge carriers. For instance, under front-side illumination, the semiconductor surface absorbs most of the light, bringing the photogenerated electron-hole pairs closer to the semiconductor/electrolyte interface. In an n-type semiconductor, this configuration shortens the diffusion path for holes to reach the surface, while electrons must diffuse through the conductive substrate, which is electrically connected to the counter electrode to facilitate the reduction reaction.

In contrast, under back-side illumination, photogenerated charge carriers accumulate mainly at the back of the semiconductor where light absorption is most intense. In an n-type semiconductor,

holes must cross the bulk to reach the interface and oxidize the redox couple, whereas electrons have a shorter path to the substrate for external conduction. The reverse behavior occurs at the p-type semiconductor/electrolyte junction. Consequently, semiconductors are typically fabricated in thin films to minimize diffusion paths. The interplay between the diffusion length, the charge carriers, and their mobilities must be evaluated when selecting the illumination mode.

Stability is a critical factor for photoelectrodes. Robust chemical stability in electrolytes, particularly under harsh conditions such as highly oxidizing or acidic environments, must be ensured. This can be assessed by immersing a semiconductor sample in the electrolyte and monitoring changes in its key properties, such as surface composition, dimensions, color, weight, and other fundamental physicochemical attributes. Notably, illumination can induce photocorrosion in ionic semiconductors, leading to decomposition and irreversible (or only partially reversible) ion dissolution into the electrolyte. Effective mitigation strategies include:

i. Introducing a physical protective barrier between the photoelectrode and electrolyte

ii. Countering photocorrosion by depositing catalysts on the surface to accelerate redox reactions or by incorporating hole sensors into the electrolyte (Hoang et al., 2012; Memming, 1984; Shalom et al., 2009).

5.4. Counter-electrode

In PRFBs, alternative electrode materials serve as counter electrodes alongside the photoelectrode or as cathodes and anodes during discharge. As with conventional RFBs, these materials must satisfy key criteria: high electrochemical activity toward both redox couple reactions, combined with a large specific surface area to reduce activation overpotential and low electrical resistivity to minimize Ohmic losses thereby enhancing voltage efficiency and power density; excellent electrolyte permeability to decrease the pumping energy required for operation at elevated current densities, robust chemical stability of the electrolyte to extend operational life, and cost-effectiveness to promote commercial adoption.

5.5. Electrolyte

The electrolyte composition plays a pivotal role in the performance and stability of PRFBs. These redox couples must meet several essential criteria. A high solubility to enable high energy and current densities, an adequate formal potential window to achieve high cell voltages, a rapid kinetics for redox reactions to support high power densities, a strong ionic conductivity to improve voltage efficiency, a minimal interactions with the solvent, supporting electrolyte, atmosphere and photoelectrode materials to ensure long-term stability, a low viscosity to minimize pumping energy requirements, a negligible light absorption within the semiconductor's operational wavelength range and a safety, affordability and abundance (Alotto et al., 2014; Ponce de León et al., 2006). Numerous reviews and book chapters have investigated suitable redox couples for PRFBs (Table 2), with ongoing advancements in redox chemistry expanding the options.

Table 2: Characteristics and main issues of common redox couples used in PRFBs

Redox Couple	Characteristic/issues
Cr^{3+}/Cr^{2+}	Hydrogen evolution (Hwang & Ohya, 1997; Jalan et al., 1981)
Cu^{2+}/Cu^{+}	Copper chloride complexes exhibit high solubility in aqueous solutions, minimal gas evolution, low cost, and support operation across a broad temperature range (Sanz et al., 2014).
Cu^{2+}/Cu	Electrolyte circulation helps mitigate challenges related to dendrite formation and passivation.
$I^{-}/I2$	Relatively low solubility of I_2 in aqueous solution (Sanz et al., 2014).
I_2/IO^{-}	IO^{-} can react with I- thus hindering the formation of I^{-} (Skyllas-Kazacos & Milne, 2011).
VO^{2+}/VO^{+}	VO^{2+} undergoes thermal precipitation at elevated temperatures exceeding 40 °C while maintaining a solubility of 2–4 M within the suitable temperature range and in the presence of an appropriate supporting electrolyte. Additionally, it exhibits oxidative and corrosive properties (Skyllas-Kazacos & Liuyue, 2016)
V^{3+}/V^{2+}	The species displays a green/violet color and is prone to hydrogen evolution. It achieves a solubility of 2–4 M within the appropriate temperature range and with a suitable supporting electrolyte, though solubility decreases significantly at temperatures below 5°C (Skyllas-Kazacos & Liuyue, 2016).

6. PRFBs as part of Morocco and Poland's energy roadmaps: Discussing

Poland and Morocco can advance their energy transitions by adopting PRFBs. In Poland, it's harder to reduce dependence on coal and improve old infrastructure because renewable energy sources like wind and solar are so unpredictable. These problems stem from outdated grid and coal pathways that are hard to change and insufficient integration of renewable energy to meet European standards. PRFBs are a flexible way to store extra energy from variable sources, ensuring a consistently reliable supply and allowing the addition of renewable energy without compromising grid stability.

Morocco, meanwhile, enjoys more than 3.000 hours of sunshine per year and has a forward-looking renewable energy plan, called the Moroccan Solar Plan (MSP), which is poised to thrive in solar systems. PRFBs can easily capture and store solar power using photoactive electrodes and redox mechanisms. This solution is effective in regions with high levels of sunshine, where production exceeds storage capacity. Additionally, the modular and decentralized design of PRFBs aligns with Poland's efforts to establish localized energy systems, such as cooperatives and community clusters, and with Morocco's efforts to bring renewable energy to remote areas not connected to the grid. PRFBs can help both countries meet their decarbonization goals, improve energy security, and reduce their dependence on foreign fossil fuels. They can store energy for longer periods, degrade more slowly than lithium-ion batteries, and directly utilize solar energy.

7. Conclusion

Photo-Redox Flow Batteries (PRFB) represent a significant technological advance that could transform the energy future of Poland and Morocco. Poland's transition to a less coal-dependent energy system is challenging due to existing infrastructure and the variability of renewable energy sources. However, PRFBs offer a flexible, scalable storage solution, helping stabilize the electricity supply and facilitate the integration of cleaner energy sources. Morocco's abundant solar energy, complemented by its strategic Moroccan Solar Plan, makes photovoltaic systems a natural solution. These systems capture sunlight directly and store it in easy-to-install solutions that provide reliable energy to remote areas that are not connected to the primary grid. Ultimately, these batteries represent much more than a technological advance; they serve to reduce carbon emissions, strengthen energy infrastructure, and diversify energy sources, ensuring a more secure and independent future for both countries.

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Author contributions

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Conflicts of interest

The author declares no conflict of interest.

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