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RECENT ADVANCES IN ELECTROCHEMICAL CELL FOR ENERGY SUSTAINABILITY

Ugwuanyi Sabastine Emeka (PhD)[1]
[1]department Of Science Laboratory Technology, Physics Option, School Of Science And Technology, Federal Polytechnic Ohodo, Enugu State. sabrophysics2@gmail.com

Abstract
Electrochemical cells (ECs) are increasingly crucial across various domains for its energy conversion, storage and energy sustainability. Electrochemical synthesis has emerged as a promising method to mitigate issues related to high energy consumption and pollution. As the global shift away from conventional energy sources continues, effective and efficient energy storage devices are becoming essential. Innovative electrochemical energy storage solutions, such as hybrid batteries, hybrid redox flow cells, and bacterial batteries, are part of the answer. These alternative configurations offer flexibility in materials and operating conditions, high energy conversion efficiency, and modular design options. Advances in all-solid-state batteries, which feature durable electrodes for extended cycles and high energy density, enable the development of long-lasting electronic and point-of-care devices. New batteries using abundant metal ions are approaching the performance levels of lithium-ion batteries, while flow batteries with engineered redox molecules and membrane-free designs are reducing costs and improving energy density. Some batteries, like carbon-neutral Li-CO2 batteries, not only store energy but also capture CO2, offering dual benefits of energy storage and carbon sequestration. This review explores recent advancements in energy storage devices, highlighting the shift from traditional to unconventional battery designs. It examines the operational flexibility, energy efficiency, and application compatibility of these technologies, emphasizing their role in promoting energy sustainability and reducing carbon footprints. This article summarizes how electrochemical cells have become essential for innovation and solving modern challenges, underscoring their importance in shaping a sustainable future.

Keywords: Electrochemical synthesis, Electrochemical cells (ECs), energy efficiency, energy sustainability, Battery

Introduction

In electrochemistry, the term "cell" is used to describe a variety of devices with different purposes, forms, and scales where electrochemical reactions occur. An electrochemical cell typically consists of at least two electrodes and an electrolyte (Covert, etal 2016). It can function either as an electricity generator through a spontaneous redox reaction or as a device that uses electricity to drive a non-spontaneous redox reaction. These cells include two electron-conducting electrodes separated by an ionic conductor (the electrolyte), and they are often connected by an electron conductor, usually a metal wire (Csala & Hoster, 2017). Electrochemical cells that generate electrical currents are known as voltaic or galvanic cells (lazard, 2019). Examples include batteries and fuel cells (Larcher & Tarascon). In these cells, chemical reactions associated with half-cell reactions lead to a shift in free energy, resulting in electricity generation (lazard, 2019). Conversely, in electrolysis cells use an external electric current to drive a chemical reaction that does not occur spontaneously (Larcher & Tarascon) . Fuel cells are a type of electrochemical cell that converts the chemical energy of a fuel (commonly hydrogen) and an oxidizing agent (often oxygen) into electricity through redox reactions (Obama, 2017). Unlike typical batteries, which contain all the necessary materials within them, fuel cells require a continuous supply of fuel and oxygen (usually from the

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air) to sustain the chemical reactions (Comello & Reichelstein, 2019). As long as these supplies are available, fuel cells can continuously produce electricity (Vuuren & Sluisveld, 2017). This makes fuel cells a valuable renewable energy source, particularly in remote areas (Irena, 2018).

Electrochemical cells are increasingly vital in tackling societal energy challenges across various sectors, including energy conversion and storage. In the energy field, electrochemical processes facilitate both energy conversion and storage, leading to the development of sustainable technologies such as batteries , fuel cells, and electrolyzers (Huggins, 2016). These advancements are crucial for integrating renewable energy sources and supporting the shift towards more sustainable energy systems. Energy is constantly needed in our daily lives, powering our gadgets, appliances, machines, and vehicles. However, effective energy storage is crucial, especially since renewable sources like sunlight and wind require intermediary storage due to their variable availability. Batteries are currently the primary solution for storing such energy, acting as a crucial link between generation and consumption (Facchini, 2017).

There are two main types of batteries: single-use, non-rechargeable batteries, and multi-use, rechargeable batteries which are known for their ability to store and release energy repeatedly, making them cost-effective and environmentally friendly (Jain, et al., 2017). These batteries are used in three major areas: transportation (including electric vehicles), portable electronics, and stationary power storage. Each application has specific requirements which details the types, applications, advantages, and disadvantages of various commercial batteries. The development of electric vehicles (EVs) heavily relies on advancements in battery technology, which faces challenges such as underdeveloped batteries and practical application issues (Zhou et al., 2016). Historically, lead-acid batteries (Pb-A) dominated the rechargeable battery market, particularly in the automotive sector, due to their significant market share. However, Pb-A batteries have limitations such as short cycle life, low energy density, and environmental concerns related to lead. As a result, lithium-ion batteries (LIBs) have become a promising alternative, offering high storage efficiency and a range of chemistries suitable for various applications (Dorotić, et al., 2019). LIBs typically consist of an anode, a cathode, a separator, and an electrolyte. During discharge, lithium ions move from the anode to the cathode, while electrons travel through an external circuit. During charging, this process is reversed [63]. Recent efforts have focused on making cathodes more sustainable and safer, leading to the commercialization of various materials such as LiNixCoyAl1−x−yO2 (NCA), LiMn2O4 (LMO), LiNi0.5Mn1.5O4 (LNMO), LiFePO4 (LFP), and LiNixMnyCo1−x−yO2 (NMC). These materials are used in electric vehicles by companies like BMW, Chevrolet, Nissan, and Tesla [66]. While Li-air and Li-S batteries are still in development, sodium-ion batteries are emerging as a potential alternative. For personal devices like smartphones, laptops, and cameras, batteries need to be compact, lightweight, and efficient. LIBs, particularly those using LMO and LiCoO2, are well-suited for these applications (Shah et al., 2018). Besides powering electronics, LIBs now also support the electricity grid by integrating renewable energy sources and enhancing transmission and distribution efficiency (Liu et al., 2020). A promising development involves replacing graphite anodes with silicon anodes. Silicon is abundant and cost-effective, offering higher storage capacity. While pure silicon anodes faced challenges, incorporating porous carbon additives has proven more successful (Kittner et al., 2017). Companies like Varta and Sila Nanotechnologies are developing composite anodes with increasing silicon content [76]. Additionally, graphene could enhance battery stability and capacity but is currently limited to smaller devices due to its structural constraints (Service, 2019).

Advancements in nanotechnology are pushing the miniaturization of batteries for microdevices and wearable technology. Lithium-ion-based micro/nano-batteries are ideal due to their small size, light weight, and high capacity (Comello & Reichelstein, 2019). Organic or polymer-based batteries, which avoid toxic metals and can be derived from renewable resources, also show promise. However, they have yet to see widespread commercial use, with Evonik Industries leading the development of printable polymer-based batteries for flexible devices (Karan, 2019). Bio-batteries, which use biofuel cells, are emerging as a clean energy solution with potential applications in various devices (Venkatesan, et al., 2017). The BeFC company has developed paper-based biofuel

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cells that are metal-free, recyclable, and compostable. With battery demand expected to rise by 2050, companies like Verkor are launching gigafactories to produce low-carbon, high-performance batteries, reducing reliance on Chinese manufacturers and creating job opportunities. Battery recycling is also crucial, with companies like NorthVolt and its subsidiary Revolt focusing on sustainable practices and recycling to minimize environmental impact and meet growing energy needs (Venkatesan, et al., 2015) .

A traditional electrochemical cell comprises two electrodes where electrons are transferred and stored chemically. A membrane or separator is needed to keep the electrodes apart. A shared ion participates in the electrochemical reactions at both electrodes, linking the two reactions. An electrolyte that facilitates the transport of this shared ion is crucial for the energy storage system (EES). This common design for energy storage is employed in batteries and fuel cells, utilizing reactants in solid, liquid, and gaseous states. Battery technology is particularly notable for its modularity and lower cost compared to other energy storage methods. However, solid-state devices with simple anode, membrane, and cathode designs face limitations due to the diffusion-controlled thickness of the electrodes, which affects energy storage efficiency at the electrode-electrolyte interface. This issue is addressed in flow batteries, where redox materials dissolved in electrolytes are circulated for better performance. In flow batteries, energy is stored and released through the redox states of liquid oxidants and reductants. The ability to circulate these liquids from large storage tanks into the energy conversion device allows for the separation of power and energy. Additionally, gaseous reactants can be used for energy conversion and storage. Hydrogen-based polymer electrolyte fuel cells (PEFCs) operate at lower temperatures (<120 °C) compared to other fuel cells. They generate electricity from hydrogen and oxygen, separated by an ion-exchange membrane, with liquid water and heat as byproducts. Hydrogen, being the most abundant element on Earth, is a fundamental component of water, hydrocarbons, and organic substances (Yuan, et al., 2018). Hydrocarbon fuels like ethanol and methanol can also be used instead of hydrogen, offering a combination of liquid and gaseous reactants for energy conversion. Despite their advantages, conventional EES devices face challenges, such as the need for components like electrodes, electrolytes, and membranes or separators, which can limit their practical applications.

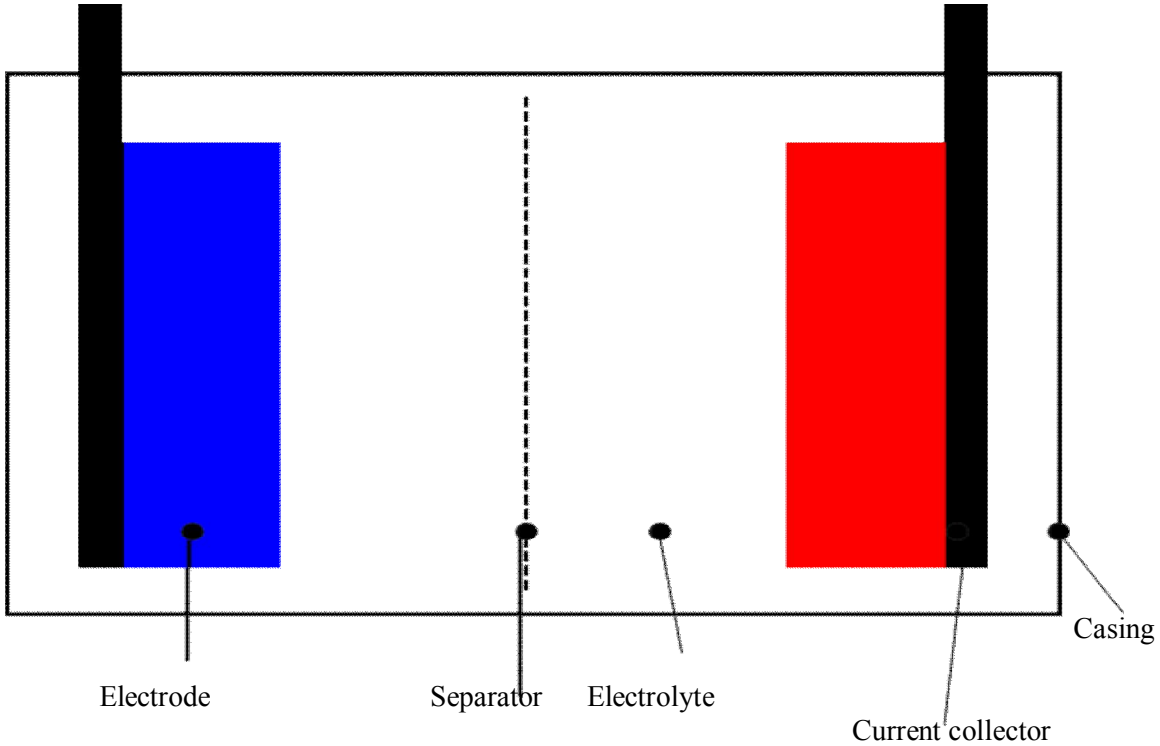

Figure 1 is the basic electrochemical cell design

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Using renewable energy across all sectors could ideally lead to zero emissions and eliminate global warming effects. However, this goal has not yet been achieved. While fossil fuels are expected to remain the primary source of global energy, renewable energy is anticipated to make a significant impact in future (Kusoglu & Weber, 2017). Accelerating the development of energy electrochemical cell to a commercially viable stage could help reach this target sooner. One of the ways to achieve this involves exploring unconventional electrochemical systems beyond conventional methods. Unconventional EES systems offer additional benefits by utilizing fewer components or integrating a mix of reactants in decentralized environments. They leverage side reactions from primary chemical processes, natural phenomena, and excess energy-carrying processes to capture and convert energy. These side reactions vary based on the system, including sources like solar radiation, wind energy, geothermal heat, ocean wave energy, microbial activity in petroleum reservoirs or marine sediments, and interactions with algae. Adopting unconventional approaches can help address rising energy demands and develop viable alternatives for energy capture and conversion, all while keeping economic considerations in mind. Although these methods present many opportunities, their unique designs and requirements pose significant challenges for mass production and commercial viability (Kusoglu, et al., 2016).

Literature Review

The evolution of voltaic cells has led to the exploration of various reactants in different states—liquid, gas, and solid—to achieve higher energy storage density. The introduction of separators or ion-selective membranes has expanded the range of usable reactants by acting as barriers for semi-solid, liquid, gaseous, and hybrid reactants. These membranes enhance system efficiency by isolating reactants and products and optimizing reactant usage. However, they also introduce performance challenges due to the ohmic resistance associated with ion transport between electrodes. For optimal electrical efficiency, membranes need high ionic conductivity, a high transference number, durability, and impermeability to gases and liquids. The membrane material should have specific functional groups or chemical compositions that selectively conduct certain ions. Perfluorosulfonic acid (PFSA) ion-exchange membranes, such as Nafion™, are commonly used in energy storage and conversion devices. They feature an ionic group (SO_3^-) attached to a fluorocarbon backbone, with mobile counter ions like H^+. Upon hydration, these membranes form a network that allows selective ion transport. The ionic conductivity of these membranes depends on their morphology and ability to maintain proper hydration. This dependency applies to various types of membranes, including polymer, polymer composite, and ceramic types. Solid polymer, copolymer, polymer blend, composite, and ceramic membranes combine the benefits of solid polymer electrolytes with filler materials but are expensive to manufacture. For example, a commercial PFSA membrane used in polymer electrolyte membrane (PEM) fuel cells costs about $600 per square meter. PFSA ionomer membranes are effective in redox environments due to their chemically stable tetrafluoroethylene backbone and balanced arrangement of polar and non-polar groups. They are more stable at higher temperatures compared to other polymer electrolytes. However, their performance and durability depend on membrane morphology. Extensive research has explored the impact of membrane morphology on ion conduction and durability(Kusoglu et al., 2017).

The PFSA variant (Nafion) was first used in a vanadium redox flow battery (RFB) in the late 1980s. Over time, ionomer membranes for redox batteries have been modified to reduce ion crossover and improve cyclability. Composite membranes have been developed to address issues with crossover and durability. These membranes are exposed to oxidative conditions to enhance resistance, particularly in RFB applications. While these modifications improve performance at higher current densities, they can reduce specific proton conductivity. Chemical and mechanical stresses from oxidizing environments can degrade the membranes, affecting ionic conductivity, water absorption, dimensional stability, and overall efficiency. In conventional electrochemical cell devices, ionomer membranes degrade over time due to chemical and mechanical stressors, resulting in loss of functionality. Research has explored various PFSA ionomer variants and alternative membrane chemistries, such as SPEEK composites, to reduce costs, improve ion selectivity, and enhance cycle life. However, these alternatives often face issues such as excessive swelling and poor mechanical properties. Specialized polymer

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blends and composites have been developed to address these challenges, but finding a universal solution remains elusive. For solid reactants, a simple porous separator can separate the anode and cathode, but these separators are not ion-selective and can allow undesirable ions to pass through. Conventional electrochemical cell technologies have used simple separators that fail when operating parameters exceed their limits. Various types of separators, including microporous, modified, composite, and non-woven types, have been employed. When separators or membranes fail, they can lead to self-discharge or crossover, resulting in performance loss. Designing membranes for RFBs requires balancing electrochemical stability and ionic conductivity in harsh environments while managing costs. The internal morphology of solid electrolytes significantly affects ionic conductivity, and understanding the distribution of hydrophobic and hydrophilic fractions is crucial. Similar challenges exist for ceramic membranes, which must manage ion conduction through vacancies and interstitials. Anion exchange membranes must compete with cation exchange membranes in terms of conductivity and chemical stability while avoiding fouling. High resistance at the electrode/electrolyte interface remains a challenge for ceramic membranes. Separators must also handle overcharge protection and significant volume expansion during charge-discharge cycles. Mathematical models considering ohmic resistance, thickness, internal morphology, pore size, and other factors are needed to develop membranes and separators with optimized electrochemical properties (Allen et al., 2015).

Challenges of Electrochemical Cell Devices

With the advancement of voltaic cells, researchers are exploring a range of reactants in various states—liquid, gas, and solid—to achieve higher energy storage densities. The introduction of separators or ion-selective membranes has broadened the range of reactants by acting as barriers for semi-solid, liquid, gaseous, and hybrid substances. These membranes enhance the efficiency of electrochemical devices by segregating reactants from products and optimizing reactant use. However, they also introduce performance losses due to the ohmic resistance encountered during ion transport between electrodes (Sadeghi-Alavijeh et al., 2016). For optimal electrical efficiency, membranes need to have high ionic conductivity, a high transference number, and durability to minimize long-term costs. They must be impermeable to gases and liquids to ensure the device operates efficiently. Membrane materials often include functional groups or chemical compositions that selectively conduct specific ions. The most prevalent ion-exchange membrane in energy storage and conversion devices is based on perfluorosulfonic acid (PFSA), where ionic groups like SO_3^- are covalently attached to a fluorocarbon backbone, and counter ions such as H^+ are mobile. When hydrated, these membranes form a network that facilitates selective ion transport. The ionic conductivity of these membranes depends on their morphology and ability to maintain proper hydration, a factor relevant to various types of membranes, including polymers, composites, and ceramics (Venkatesan, 2017).

Solid polymer, copolymer, polymer blend, composite, and ceramic membranes combine the benefits of solid polymer electrolytes with filler materials, but their high production costs make them expensive. PFSA ionomer membranes are known for their resistance to electrochemical stress due to their stable tetrafluoroethylene backbone and well-balanced polar and non-polar groups. Their phase-separated structure also allows them to perform well at higher temperatures compared to other polymers (Khorasany et al., 2015) . The performance and longevity of proton exchange membrane fuel cells (PEFCs) using PFSA membranes depend on the membrane's morphology. Extensive research has focused on the impact of ionomer morphology on conductivity and durability. The first vanadium redox flow battery (RFB) using PFSA (Nafion) was developed by Skyllas-Kazacos in the late 1980s. Since then, PFSA ionomers have undergone various morphological modifications to reduce ion crossover and enhance cyclability. Composite Nafion membranes have been developed to address these issues, improving performance at higher current densities but often at the expense of proton conductivity. Oxidative and physical stresses can degrade these membranes, leading to decreased ionic conductivity, water uptake, and changes in morphology. Over time, ionomer membranes in conventional energy storage devices degrade due to chemical, mechanical, or combined stressors, which affects their proton conductivity, water absorption, and dimensional stability. Various PFSA ionomer variants and alternative membrane chemistries, such as SPEEK-

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based composites, have been investigated to address issues like cost, ion-selectivity, and crossover (Vijayakumar et al., 2016). However, these alternatives often suffer from excessive swelling or poor mechanical properties. Specialized membranes like long side-chain polybenzimidazole and polymer blends have shown improvements in reducing ion crossover and dendrite formation, but finding a universally compatible membrane remains challenging. The high costs of membrane manufacturing, their degradation, and limited operational ranges continue to be significant issues.

For solid reactants, using a simple porous separator between the anode and cathode is effective, though these separators are not ion-selective and can suffer from performance issues if their physical integrity is compromised. Early energy storage technologies with such separators failed when exceeding operational parameters like temperature and current density. Modern separators come in various forms, including microporous, modified, composite, and non-woven types. When a separator's physical integrity is lost, it can lead to performance losses due to self-discharge or crossover. Designing membranes for RFBs requires balancing electrochemical stability and ionic conductivity in oxidizing and reducing environments without significantly raising costs. Understanding how hydrophobic and hydrophilic fractions affect membrane properties is crucial. Ceramic membranes also face challenges such as high resistance at the electrode/electrolyte interface. Membranes and separators must offer overcharge protection and handle significant volume changes during charge-discharge cycles. Developing mathematical models that account for ohmic resistance, thickness, morphology, pore size, and mechanical strength is essential for optimizing membrane and separator performance and safety in energy storage systems.

Methodology

The methodology used was content analysis as this is review work with deep current literature search to dig up the current state of electrochemical cell development.

Results

TEMPO-Based Electrolytes**: The combination of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) with phenazine for symmetric aqueous RFBs has shown a redox potential of 1.2 V. The functionalization of TEMPO with various groups has enhanced solubility and performance. Methyl Viologen and TEMPO: A methyl viologen anolyte paired with a TEMPO catholyte in a neutral supporting electrolyte has demonstrated high current densities and impressive cycling performance. PEGylation of viologen further improved solubility and reduced crossover, resulting in near-total capacity retention over 500 cycles. Quinone-Based Electrolytes: Quinones are known for their high specific capacity and redox activity. For example, diaminoanthraquinone (DAAQ) derivatives and anthraquinone-2-sulfonic acid have shown promising results. These organic redox species benefit from modifications that increase solubility and alter reduction potentials, though they also face challenges like multi-electron reduction potentials and pH-dependent behavior. Hybrid Redox Electrolytes: Combining organic and metal-based electrolytes can yield promising results. For instance, the use of tungsten-based POMs with hydroquinone has achieved a specific energy density of 20 Wh kg^{-1}. Similarly, combining anthraquinonedisulfonic acid with iron sulfate has made large-scale energy storage more cost-effective. Semi-Solid Electrolytes: To overcome solubility limits, semi-solid redox electrolytes are being explored. For example, lithium-organic nanocomposite suspensions and silicon-coated carbon particles as semi-solid electrolytes have shown high volumetric capacity and improved performance.

Conclusions and Recommendations

1. Molecular Weight and Conductivity: High molecular weight of metal-free redox species can hinder rapid solubility and conductivity, especially in non-aqueous electrolytes. Innovations in molecular engineering and solvent systems are necessary to address these issues.
2. Energy Density and Cost: While metal-free electrolytes offer sustainability, achieving competitive energy densities and costs remains a challenge. Advances in organic redox molecules, cell designs, and electrode efficiency are needed to improve performance.

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3. Self-Discharge and Stability: Ensuring low self-discharge rates and long-term stability of metal-free redox electrolytes is crucial for practical applications. Research into more stable and durable materials is ongoing should continue.
4. Integration with Existing Technologies: Future RFB technologies may integrate semi-solid/solid reactants and hybrid designs to compete with traditional Li-ion batteries in terms of cell voltage and cost. In conclusion, metal-free redox electrolytes present a promising avenue for sustainable and cost-effective energy storage solutions. Ongoing research and development are focused on addressing their limitations, improving their performance, and making them viable alternatives to metal-based systems.

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