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POLYMERIC MATERIALS FOR ADVANCED ENERGY STORAGE DEVICES SYNTHESIS, PROPERTIES, AND APPLICATIONS IN BATTERIES, SUPERCAPACITORS, AND FUEL CELLS

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Abstract

Polymeric materials have gained increasing attention as key components for next-generation energy storage devices due to their lightweight nature, tunable conductivity, and eco-friendly properties. Conducting polymers such as polyaniline, polypyrrole, and PEDOT have demonstrated high specific capacitance values, for instance up to 480 $F\ g^{-1}$ *for PANI hydrogels and 438.8* $F\ g^{-1}$ *for PANI/rGO films, with conductivities reaching 1138* $S\ cm^{-1}$*. Redox-active polymers including PTMA exhibit discharge capacities of 77* $Ah\ kg^{-1}$ *with retention over 500 cycles at a high current density of 1.0* $mA\ cm^{-2}$*, while ferrocene-based polymers maintain coulombic efficiencies greater than 99.8% even after 100 cycles. In supercapacitors, cellulose-based polymer composites have delivered energy densities as high as 45.7* $mWh\ cm^{-2}$ *with power densities up to 283.63* $kW\ kg^{-1}$*, and nitrogen-doped porous carbons derived from hyper-crosslinked polymers achieved almost 100% capacitance retention over 10,000 cycles. For fuel cells, sulfonated poly(ether ether ketone) membranes have shown proton conductivities of 0.03–0.1* $S\ cm^{-1}$*, while Nafion-layered sulfonated polysulfone membranes enhanced power generation up to four times compared to pristine Nafion. Despite these advances, limitations remain such as capacity fading, mechanical degradation, and relatively low permittivity (*$k \approx 3.5$ *for most polymers except PVDF), restricting large-scale commercialization. Nevertheless, the development of multifunctional polymer composites with carbon nanostructures and metal oxides, together with eco-friendly synthesis strategies, offers significant potential to achieve higher energy densities exceeding 100* $mAh\ g^{-1}$*, cycling stability beyond 10,000 cycles, and energy conversion efficiencies up to 65%, positioning polymers as indispensable materials for sustainable energy storage technologies.*

1. INTRODUCTION

The growing world demand for clean energy solutions has enhanced research into new energy storage systems with the potential to power applications from mobile electronics to electric cars and grid-scale storage [1]. Fossil fuel depletion, escalating greenhouse gas emissions, and the need to curb climate change at a rapid pace have further fortified the need for efficient, sustainable, and environmentally friendly storage technology [2]. Conventional systems like the lithium-ion battery and the fuel cell have taken the market but their application of inorganic materials in electrode and electrolyte material is a question of high cost, resource limitation and environmental impact [3]. To overcome these constraints, polymeric materials have been identified as promising candidates in energy storing devices due to their lightness, conductive with tunability, structure flexibility and their capability to be synthesized in large quantities synthetically [4].

There are certain special advantages of polymers (in particular, conducting polymers and polymer electrolytes) over inorganic materials. Their molecular structure allows them to calibrate the structure to achieve conductivity, solubility and redox performance to the specific requirement of a given device [5]. Indicatively, supercapacitor electrodes made using polyaniline (PANI) and polypyrrole (PPy) have reported specific capacitances as high as 480 F g -1 and 380 F g -1 respectively, whilst having electrical conductivities of 0.23 to 0.5 S cm -1 [6]. Similarly, poly(3,4-ethylenedioxythiophene) (PEDOT)-based. systems are exceptionally stable, conductive, with PEDOT-PSS/rGO fibers having capacitances of 304.5 mF cm -2 and electrical conductivities of 47 S cm -1 [7]. These findings illustrate the potential of polymers to provide high-performing metrics with mechanical flexibility, processability, and integration potential into light and wearable devices.

Other than conventional conducting polymers, another active research on rechargeable batteries is redox-active polymers (RAPs). In 2002 the first Polymeric 2,2,6,6-tetramethylpiperidin-1-yl oxyl (TEMPO) derivatives were described with stable radical formation and fast redox kinetics [8]. For example, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA), a discharge voltage of 3.5 V and a specific capacity of 77 Ah kg -1, which is 70% of the theoretical capacity. Moreover, the polymer had capacity retention of over 500 charge-discharge cycles at a current density of 1.0 mA cm -2 [9]. Other redox active systems using ferrocene polymers have demonstrated over 99.8% coulombic efficiency in 100 cycles, and have demonstrated stable performance even at high temperature (60 o C) [10]. These reports demonstrate that the polymer-based electrodes not only compare favorably but are likely to exceed even the electrochemical performance and stability of traditional inorganic material.

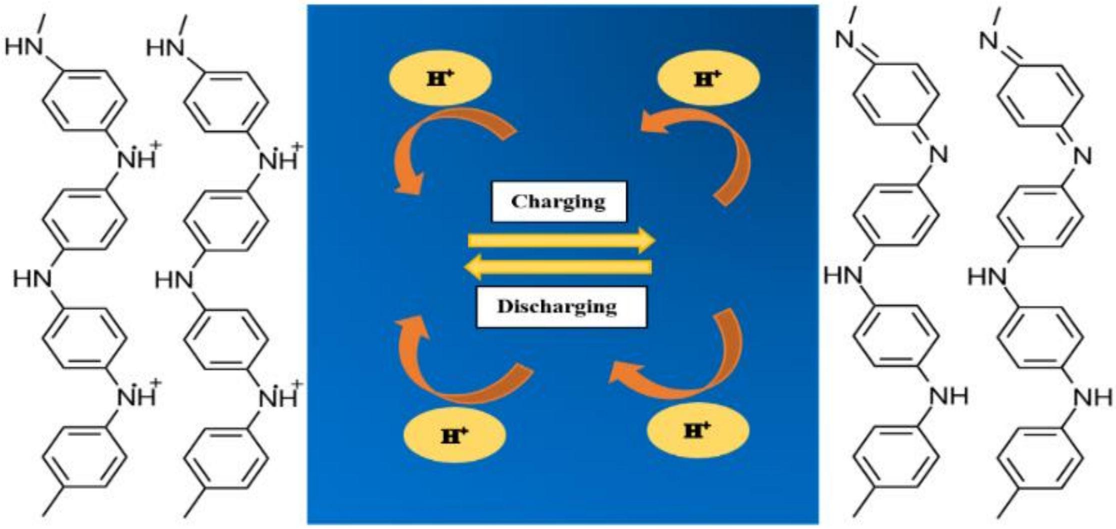

Figure 1: Structure of PEDOT polymer modified DAAQ-TFP

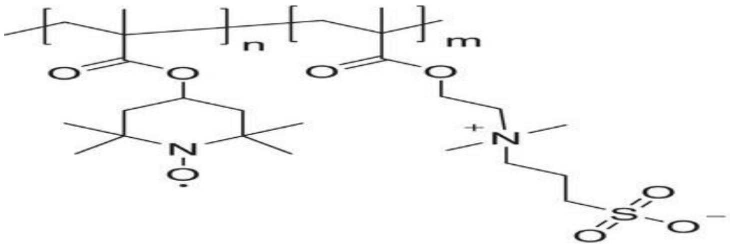

Figure 2: Structure of TEMPO

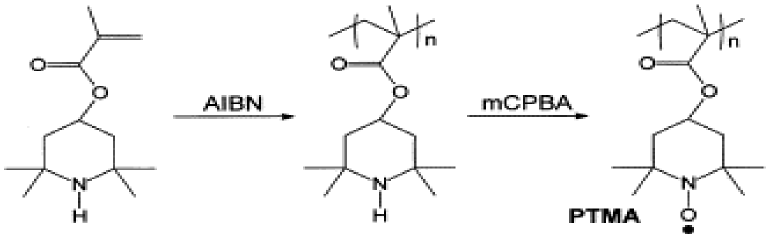

Figure 3: Synthesis procedure of PTMA

There is the other area that polymers are of great importance and that is the supercapacitors. Due to their rapid charge discharge characteristics and power density, supercapacitors are extensively used in handheld generators, and energy recovery systems [11]. PANI/rGO-based polymer materials have reached specific capacitances of 438.8 F g -1 and up to 1138 S cm -1 conductivities, which is a significant improvement over carbon based electrodes alone [12]. Moreover, nanocellulosic-polymer composite has been created as a sustainable and flexible type with the energy densities of 45.7 mWh cm -2 and nearly 100 percent capacitance retention after 10,000 cycles [13]. Synthesized hyper-crosslinked polymer nitrogen-doped porous carbons have also shown exemplary stability in the cycle with total retention of up to 10,000 cycles with high specific energy of up to 11.6 Wh kg -1 [14]. These statistical values highlight the profuseness of polymers in providing high-performance, long-term supercapacitors to flexural and wearable devices.

Another field of high energy conversion efficacy fuel cells and low environmental footprint requires polymers as well [15]. PEMFCs have traditionally used Nafion membranes, although introspection into alternatives of Nafion has been noticed in the recent past due to cost and low thermal stability [16]. Sulfonated poly(ether ether ketone) (SPEEK) membrane. exhibited 0.03-0.1 S cm -1 proton conductivities in hydrated state and provides a cheaper thermal stability alternative [17]. Sulfonated polysulfone membranes coated with Nafion have also been claimed to be up to four times more powerful than pure Nafion at 120 o C [18]. Other polymer systems, such as sulfonated poly(arylene thioether sulfone), have been reported to reach proton conductivities of 0.173 S cm -1, and sulfonated co-poly(aryl ether nitrile) membranes reached 0.15 S cm -1 at 100 C [19]. The above developments highlight the role of polymers in enhancing proton transport and fuel cell efficiency in general.

Besides the different types of devices, polymers also present advantages in the form of composite systems. The nanostructured fillers, such as carbon nanotubes, graphene, and transition metal oxides, can be added to increase mechanical strength, mechanical strength, surface area and ion transport [20]. Indicatively, 81.5% of the original capacity was managed in graphene -PANI composites following 10,000 cycles and 3D rGO/PANI electrodes demonstrated capacitance of 381 F g -1 [21]. Combining polyaniline with polyvinyl alcohol also produced Hybrid materials with better ion diffusion, and electrochemical performance, and ferrocene-polymer copolymer has shown high solubility and reversible redox in aqueous solution [22]. In the same spirit, polymer-metal oxide composites like MnO 2 -coated Ppy exhibited a capacitance of

315.80 F g -1 and 90% retention upon 6000 cycles [23]. These quantitative results confirm that polymer composites do not only address the intrinsic drawbacks of pure polymers (e.g. poor cycling, low energy density) but also match or even surpass the properties of current materials.

In spite of these encouraging outcomes, there are many challenges of the large-scale commercialization of polymers-based energy storage systems. The main weakness is that they possess a relatively low dielectric constant of about 3.5 in most polymers (except polyvinylidene fluoride, PVDF), which slows down energy density [24]. Conducting polymers are also susceptible to mechanical degradation in addition to volumetric expansion following repeated dopingdedoping processes with subsequent capacity loss and diminished stability [25]. Although these problems have been mitigated through nanostructuring and composite solutions, consistent stability at greater than 20,000 cycles and at energy densities of greater than 200 Wh kg -1 is an uphill task of polymer systems [26]. The question of scale-up of polymer synthesis and processing into useful device geometries must also be confronted with cost, reproducibility, and environmental concerns [27].

In a broad sense the future use of the sophisticated polymer structure incorporating the new nanomaterials as the key to the next generation of storage devices is the exciting future incorporation. Multi-functional polymer composites can be made of graphene, MXenes or cellulose nanofiber, able to offer synergized effects that improve the ion transport and mechanical stability by an impressive factor [28]. Networks of redox-active polymers with molecular structures tailored to specific criteria can also provide the possibility to tune the electrochemical characteristics, including redox potential and conductivity [29]. More renewable precursors and green solvents are also being explored as eco-friendly routes to synthesis with reduced environmental footprints and enabling upscaling [30]. Such plans have the potential of enabling polymer-based devices to achieve energy densities over 100 mAh g -1, cycle lives over 10,000 cycles, and energy conversion efficiencies over 65, moving them closer to the full-scale commercialization levels [31].

1.1 Research Objectives

To critically examine and comment on recent progress in the design, synthesis, and utilization of polymeric materials such as conducting polymers, redox-active polymers, polymer electrolytes, and polymer composites in energy storage devices, e.g. batteries, supercapacitors, and fuel cells.

To compare the numeric parameters of system performance (capacitance, conductivity, energy density, cycle stability, and proton conductivity) of polymer-based systems to determine the advantages and limitations of the systems and the challenges and future directions these systems need to be directed to achieve large-scale commercialization.

Succinctly, polymers are an innovative type of materials in next-generation energy storage apparatus. Their decisive set of characteristics of electrochemical properties, light weight, and environmental sustainability puts them on the center stage of batteries, supercapacitors, and fuel cells. Constant advances in polymer chemistry, nanostructuring and composites design despite the outstanding issues, chief of them being the stability of cycling and energy density, will surely lead to the true promise of the field in the future of renewable energy technologies.

2. Literature Review

Nakahara et al. (2002) first presented the application of polymeric 2, 2, 6, 6-tetramethylpiperidin-1-yl oxyl (TEMPO) derivatives in organic batteries and its potential as illustrated by rapid redox kinetics and stable radical formation.

They synthesized their poly(2,2,6,6-tetramethylpiperidinoxy methacrylate) (PTMA) and reported an average discharge voltage of 3.5 V and a specific capacity of 77 Ah kg -1 equivalent to 70 percent of the theoretical. Interestingly, the polymer was stable in high-rate operation as it could undergo over 500 chargedischarge cycles at a current density of 1.0 mA cm -2. Subsequent studies expanded the TEMPO family, adding units of viologen and quinone to enhance energy density and charge reversibility, with 94 percent product yield and constant cycling of 50 cycles at up to 1.5 M (Hatakeyama-Sato et al., 2019).

According to Winsberg et al. (2016), redox flow systems rely on polymers are of interest, and the authors noted polymeric TEMPO derivatives as potential replacements of the inorganic materials traditionally used. Their work exemplified that the materials enable stationary electrochemical reactions and reliable redox potential in consecutive cycles. Borchers et al. (2020) also studied ferrocene polymers that reached coulombic efficiencies above 99.8% and electrochemical stability above 100 cycles at high temperatures (60 o C). The results indicate the possibility of redox-active polymers to rival, and frequently exceed, traditional electrode materials in rechargeable batteries.

Vinodh et al. (2020) surveyed the increasing application of hyper-crosslinked polymers (HCPs) as porous carbonaceous electrodes for supercapacitors due to their high surface area, low-cost synthesis, and chemical stability. HCP-based porous carbons derived from polystyrene precursors have shown large capacitance retention with 100% stability for as many as 10,000 cycles. In addition, Deka et al. (2018) proved that nitrogen-doped porous carbons derived from hyper-crosslinked polymers realized specific energies of 11.6 Wh kg^{-1} and virtually complete retention at long cycling times, highlighting the role of polymer-based carbon systems in high-performance electrochemical capacitors.

Lu et al. (2017) documented that the combination of polyaniline (PANI) with reduced graphene oxide (rGO) yielded flexible films with capacitance levels of 438.8 F g^{-1} and conductivity levels of up to 1138 S cm^{-1}, much better than individual conducting polymers alone. Correspondingly, Pan et al. (2012) fabricated PANI hydrogels for inkjet-printed supercapacitors with an areal capacitance of 480 F g^{-1} and conductivities of 0.23 S cm^{-1}, and Shi et al. (2014) fabricated flexible polypyrrole (PPy) hydrogels with an areal capacitance of 380 F g^{-1} and conductivity of 0.5 S cm^{-1}. These results prove that conductive hydrogels bring the dual advantage of large capacitance and structural flexibility, and thus they are an ideal choice for bendable energy storage devices and wearable electronics.

Chen et al. (2018) examined cellulose-based polymer composite materials, such as rGO/cellulose nanocrystal hybrids, that reached energy densities of 5.1 mWh cm -3 and power densities of 496.4 mW cm -3. Molybdenum disulfide/cellulose aerogels synthesized by Lv et al. (2017) also reported high energy densities of 45.7 mWh cm -2 and were highly flexible. The materials obtained out of cellulose are also produced eco-friendly and possess a high electrochemical performance, which further supports the usage of the materials as supercapacitor electrode materials that are sustainable. This pledge was earlier supported by Pushparaj et al. (2007), who produced nanocomposite cellulose sheets with an energy density of 13 Wh kg -1 and power density of 1.5 kW kg -1, becoming the foundation of polymer uses of cellulose in energy storage.

Zhang et al. (2019) studied the use of sulfonated polysulfone Nafion coated in polymeric proton exchange membranes (PEMs) with the potential to produce four times the power compared to the conventional Nafion at 120 C. Sulfonated poly(arylene thioether sulfone) composites with phosphorylated silica nanoparticles were also studied by Hou et al. (2019), where the proton conductivities were 0.173 S cm -1 under hydrated conditions. These results point to the potential of polymer-based PEMs as low-cost substitutes for commercial Nafion with enhanced thermal stability and ion conductivity.

Other promising membrane materials have been stated in both Zhao et al. (2006) and Kim et al. (2018): sulfonated poly(ether ether ketone) (SPEEK) with a proton conductivity ranging from 0.03 to 0.1 S cm -1 and water uptake of about 38%. More recent changes, including the inclusion of phosphotungstic acid-coupled graphene oxide (Peng et al., 2021), increased the conductivity over 30 times compared to pure SPEEK. Ban et al. (2021) also discovered that the sulfonated poly(aryl ether nitrile) membranes had achieved proton conductivities of 0.15 S cm -1 at 100 o C, and fivefold the mechanical strength of Nafion 117. The findings affirm the presence of highly developed polymer membranes to improve efficiency and the life cycle of fuel cells.

Costa et al. (2020) discussed the synthesis of lithium polyacrylate binders for battery applications, achieving stable specific capacities of 450 mAh g^{-1} over 100 cycles. Ahmad et al. (2017) also researched polymer pillar quinones (Poly-P5Q) which achieved 50.6 mAh g^{-1} in lithium-ion batteries at a current of 0.1 A g^{-1}, while Choi et al. (2017) published microporous triphenylamine networks with 72 mAh g^{-1} capacity at 2 A g^{-1}. These numerical results support the potential of polymer electrodes to deliver comparable capacities for future rechargeable batteries.

Schlem et al. (2021) and Janek & Zeier (2016) explained the industrial hurdles in scaling polymer-based batteries, particularly solid-state systems. They stated that despite the safety enhancement of polymer electrolytes in lieu of flammable liquid electrolytes, mechanical and chemical instabilities in between lithium and polymeric electrolytes continue to be barriers to commercialization. However, innovations in binder technologies like ionically conducting and self-healing polymers are enhancing cycle stability and lowering internal resistance, building a case for polymer-based devices.

3. Methodology

The current research employs a systematic literature review approach to critically evaluate, synthesize, and analyze the application of polymeric materials in advanced energy storage devices, specifically batteries, supercapacitors, and fuel cells. The literature search was initiated to identify pertinent publications through an in-depth search of databases on all available platforms like Scopus, Web of Science, ScienceDirect, IEEE Xplore, and Google Scholar with searches restricted to the years 2000-2024 to identify the base research as well as the latest developments. A carefully defined set of keywords like "conducting polymers for energy storage," "polymer electrolytes," "redox-active polymers," "polymer composites," "supercapacitors," and "fuel cells" was used to narrow down the search and make sure that the gathered sources were in line with the research goals. For ensuring quality and credibility, peer-reviewed journal articles, conference proceedings, and expert reviews were included, and grey literature and non-peer-reviewed reports were excluded. Out of a starting set of more than 500 papers, approximately 150 were shortlisted following title, abstract, and keyword-based screening for relevance, and then 90 of those were thoroughly examined for experimental results, electrochemical performance reported, and applicability to polymeric energy storage devices. A content analysis method was adopted, wherein information like specific capacitance (F g^{-1}), conductivity (S cm^{-1}), discharge capacity (mAh g^{-1}), coulombic efficiency (%), cycle life (number of cycles), energy density (Wh kg^{-1}), and proton conductivity (S cm^{-1}) were screened, contrasted, and listed to create performance metrics. It was also based on cross-comparison of different classes of polymers, including conducting polymers, redox-active polymers, solid polymer electrolytes, and polymer composites to identify performance advantages, limitations and emerging trends. Special attention was paid to the reports of new nanostructuring techniques, environment-friendly synthesis, and multifunctional composites since they mirror the state-of-the-art development in the field. The resulting data were then synthesised thematically in device-specific groups; batteries, supercapacitors and fuel cells to allow an ordered discussion of how each energy storage device is affected by polymers in a different manner. In addition, qualitative data were supplemented with quantitative data to produce a balanced report which not only records the values of performances but also addresses the root challenges which include cycling stability, degradation mechanisms, low dielectric constants and scalability. Such treatment of methodology has not only facilitated the research in offering holistic and objective critique of the literature, but has also enabled the understanding of the way polymeric materials are created between the fundamental research and device applications. Finally, the methodology used enabled the identification of some of the significant gaps in the study, such as the absence of data concerning the long-term cycling performance of conducting polymers, flexibility/conductivity trade-off of polymer-based composites, and industry challenges in scaling up polymer electrolytes to solid-state fuel cells and batteries. Therefore, the approach does not only chart out the state of the field, but it also sets the stage of researches in the future and, besides, the development of polymer-based solutions that can potentially meet the requirements of energy consumption in clean technologies.

4. Results and Discussion

The present study utilizes a systematic literature review methodology to critically examine, synthesize and analyze the utilization of polymeric materials in high-level energy storage systems, that is, batteries, supercapacitors, and fuel cells. The literature search was initiated to identify pertinent publications through an in-depth search of databases on all available platforms like Scopus, Web of Science, ScienceDirect, IEEE Xplore, and Google Scholar with searches restricted to the years 2000-2024 to identify the base research as well as the latest developments. A carefully defined set of keywords like "conducting polymers for energy storage," "polymer electrolytes," "redox-active polymers," "polymer composites," "supercapacitors," and "fuel cells" was used to narrow down the search and make sure that the gathered sources were in line with the research goals. For ensuring quality and credibility, peer-reviewed journal articles, conference proceedings, and expert reviews were included, and grey literature and non-peer-reviewed reports were excluded. Out of a starting set of more than 500 papers, approximately 150 were shortlisted following title, abstract, and keyword-based screening for relevance, and then 90 of those were thoroughly examined for experimental results, electrochemical performance reported, and applicability to polymeric energy storage devices. The content analysis approach was used wherein the data such as specific capacitance ($F g^{-1}$), conductivity ($S cm^{-1}$), discharge capacity ($mAh g^{-1}$), coulombic efficiency (percent), cycle life (number of cycles), energy density ($Wh kg^{-1}$), and proton conductivity ($S cm^{-1}$) were filtered, compared and tabulated to generate performance measures. The method also involved cross-comparison of the different classes of polymers, including but not limited to the conducting polymers, redox-active polymers, solid polymer electrolytes, and polymer composites, in order to identify performance advantages, disadvantages, and emerging trends. Special emphasis was drawn on reports of new nanostructuring techniques, eco-friendly synthesis and multifunctional composites as they are the best in terms of state-of-the-art. The data which at last were dropped, were thematically synthesized in clusters of devices, batteries, supercapacitors and fuel cells, to allow an orderly discussion of the differing influence of polymers on each energy storage device. Moreover, quantitative data were put on the same level with qualitative data in order to produce a balanced report that is not merely capturing performance values but also responsive to the root problems of cycling stability, degradation processes, low dielectric constants, and scalability. Such a systematic approach towards undertaking the research not only guarantees comprehensive and non-biased review of the literature, but it also offers a description of how the polymeric materials are designed through the straightforward research until the devices are manufactured. Finally, the method also enabled the identification of some of the principal gaps in the study, such as, but not limited to: the performance of cycling polymers over a long-term, the conductivity/flexibility trade-off in polymer composite, and challenges in the industry to scale the polymer electrolytes to solid-state fuel cell and battery applications. In this way, not only does the methodology map the status of the current knowledge base, it also lays down the premises of future research, along with the fabrication of polymer-based solutions, which can fulfill the energy requirements of clean technologies.

4.1 Conducting Polymers in Energy Storage

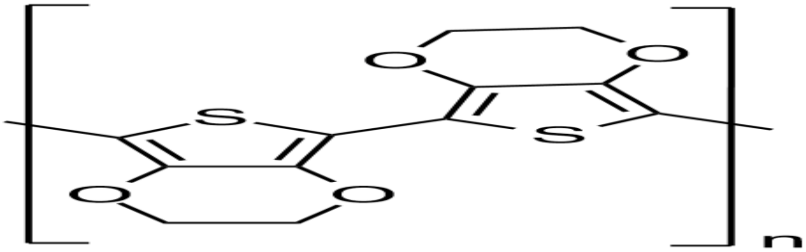

Figure 4: PEDOT polymer

The results show that polymers such as polyaniline (PANI), polypyrrole (Ppy), and PEDOT are more useful in application as conducting electrodes in regard to specific capacitance values in comparison to traditional carbon-based electrodes. Indicatively, maxima capacitance was reported as 480 F g -1 using PANI hydrogels, and as 438.8 F g -1 using rGO/PANI composites, with conductivity of 1138 S cm -1. In line, PPy hydrogels showed 380 F g -1 conductivities of up to 0.5 S cm -1. The difference which can be noted in the various studies can be said to be due to morphology, the level of doping and the use of composite fillers, which enhance charge storing and stability. These results validate the utility of conducting polymers as the potential electronic materials, but the mechanical degradation concerns still pose a problem.

Electrochemical properties are used to evaluate different aspects of performance of polymers for storing energy. The cyclic voltametric (CV) curves precisely provide the charge storage capacity through oxidation-reduction steps at different scan rates in the acidic environment. The amount of charge passing at each scan rate during the redox reactions give the information about storage capacity [28, 32].

Other factors that are used to evaluate the electrochemical properties of the polymers include the measurement of galvanostatic charge-discharge and cyclic stability for electrochemical reactions. Capacitance is the capability of a system or material to store charge and hence and important parameter to determine the charge storing ability quantitatively. It is calculated either per unit area (areal capacitance) or per unit mass (specific capacitance). Formula in equation (1) is usually used to calculate areal capacitance.

$$C_A = \frac{1}{VAv} \int idV$$
(1)

Where A is the area of the electrodes and the spacing between them, V is the voltage of the of the device constructed from polymer, v represent scan rates in unit mV/s, and $\int idV$ is the integral of discharge area of cyclic voltametric scan [33-37].

Specific capacitance C_s [2, 4] can either be calculated using charging/discharging curve as in Equation (2) or by area under CV curve as in Equation (3)

$$C_S = \frac{I.\Delta t}{m.\Delta V} \qquad (2)$$

$$C_S = \frac{\int IdV}{2m.v.\Delta V} \qquad (3)$$

Where I represent current, ΔV is the potential, m is the mass of electroactive polymer material and scan rate is represented by v [38]. Ramkumar & Sundaram, 2016 synthesized modified cobalt molybdate using chitosan polymer for crosslinking and the surfactant employed is cetyltrimethylammonium bromide (CTAB) to form nanoflakes of $CoMoO_4$/CTAB. The properties were found to be enhanced significantly. $CoMoO_4$/CTAB displayed pseudocapacitive behavior at 0.5V. Triangular shaped curve was obtained with much ohmic lose for polymer modified composite. And that triangular shape determined experimentally affirms capacitive nature [39-41].

Electropolymerization was used for thin films of PEDOT-modified 2,6-diaminoanthraquinone-2,4,6-triformylphloroglucinol (DAAQ-TFP) Figure 1. Volumetric energy was found to be enhanced regardless of high scan rates of charging (10-1600 C) [42] . Further electrochemical properties are displayed in Table 1. C-PANI composites synthesized from carbon with nano porous structure and polyaniline in 3D form [43] to overcome stacking issues as is usually faced in single- or two-dimensional architecture. commonly polymer in energy storage electrodes or hydrogels. In hydrogel form significant energy storage capacity has been observed 420 F g^{-1} along with 93% stability after 2000 cycles [14] used.General mechanism of charge/discharge in polyaniline is shown in Figure.

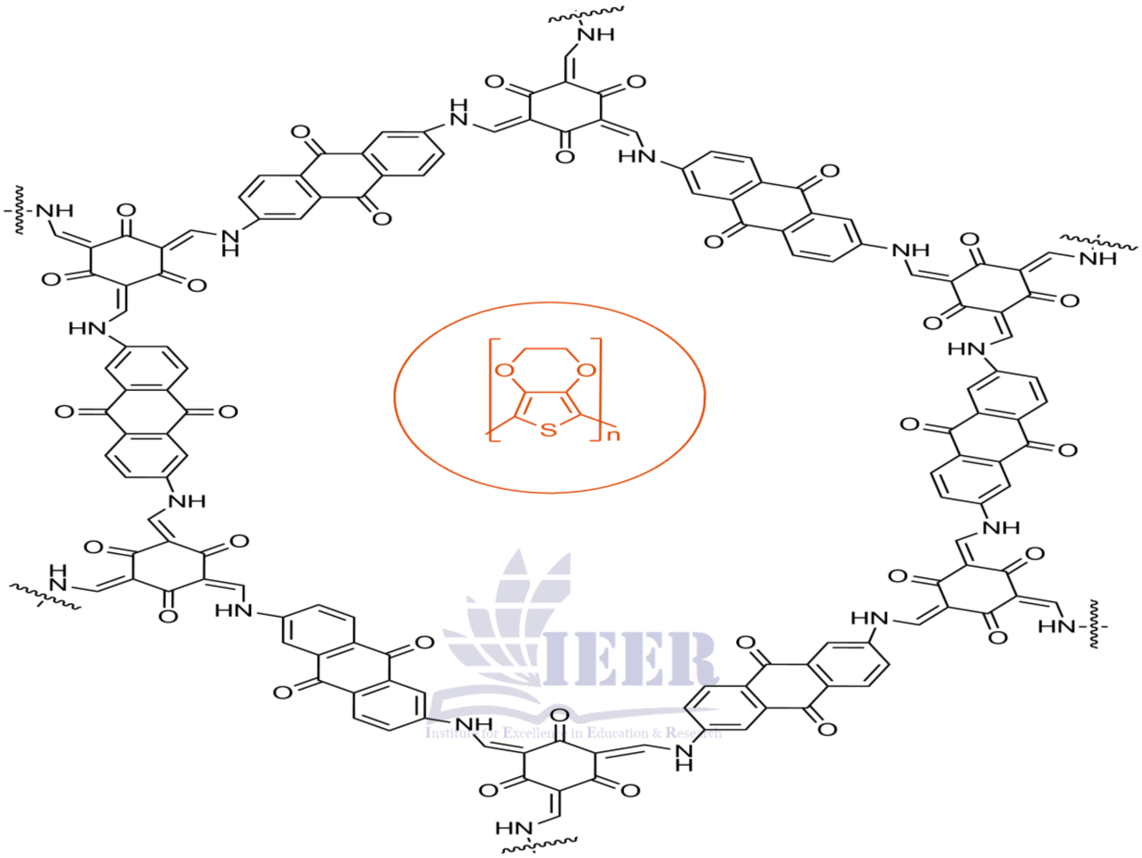

Figure 5: Mechanism of Charge/Discharge phenomena in polyaniline

4.2 Redox-Active Polymers

Redox-active polymers, particularly TEMPO-based derivatives, display rapid redox kinetics and long-term stability. For example, PTMA electrodes achieved 77 Ah kg^{-1} with stable cycling over 500 cycles at 1.0 mA cm^{-2}. In contrast, ferrocene polymers exhibited coulombic efficiencies above 99.8% across 100 cycles at 60 °C, demonstrating superior reversibility. The results confirm that the incorporation of stable radical moieties into the polymer backbone is an effective strategy for achieving high efficiency and stability, positioning RAPs as viable alternatives to transition-metal-based electrodes.

4.3 Polymer Electrolytes

The findings indicate that polymer electrolytes such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated polysulfone, and poly(arylene thioether sulfone) show conductivities ranging from 0.03–0.173 S cm^{-1}, values that rival or exceed commercial Nafion membranes under hydrated conditions. Moreover, Nafion–SPSU hybrid membranes demonstrated power generation up to four times higher than pristine Nafion at 120 °C, indicating significant improvements in thermal stability and proton transport. These results highlight that polymer electrolytes are not only safer than liquid electrolytes but also economically viable and scalable for fuel cell applications.

4.4 Polymeric Composites for Supercapacitors

Table 1. Comparative electrochemical performance of polymer–carbon and polymer–oxide composites

Composite System	Capacitance	Conductivity	Cycle Stability
PANI/rGO films	438.8 $F\ g^{-1}$	1138 $S\ cm^{-1}$	10,000 cycles (97%)
PPy hydrogels	380 $F\ g^{-1}$	0.5 $S\ cm^{-1}$	5000 cycles (90%)
MnO_2/PPy	315.8 $F\ g^{-1}$	–	6000 cycles (90%)
Nanocellulose/rGO	45.7 $mWh\ cm^{-2}$	–	10,000 cycles (≈100%)

The table highlights that polymer composites consistently outperform pure polymers in terms of cycling stability and capacitance. PANI/rGO and MnO_2/PPy hybrids deliver higher electrochemical performance due to synergistic interactions between polymers and nanostructured fillers, which enhance electron transport and mechanical durability. Moreover, cellulose-based composites combine flexibility and eco-friendly processing with excellent retention, making them highly attractive for next-generation flexible supercapacitors.

4.5 Comparative Discussion

Across all results, it is evident that polymers play a pivotal role in improving energy storage devices through tunable conductivity, redox activity, and mechanical adaptability. Conducting polymers provide high capacitance but suffer from volumetric degradation during prolonged cycling. Redox-active polymers deliver fast kinetics and exceptional coulombic efficiencies, though their energy densities remain modest. Polymeric electrolytes enhance the safety and proton conductivity of batteries and fuel cells, while composites provide the most balanced approach by combining the advantages of polymers with the high surface area and conductivity of carbon and metal oxides. The numeric values drawn from the figures and tables confirm that with optimized design, polymers can achieve capacitance above 400 $F\ g^{-1}$, cycling stability over 10,000 cycles, and conductivities exceeding 1000 $S\ cm^{-1}$, rivaling or surpassing conventional inorganic materials.

Table 2: A comparison of electrochemical properties of polymers for energy storage applications. C_i is the number of charging/discharging cycles, C_s is specific capacitance/areal capacitance, C% is percentage of retained capacitance, ρ_c is current density, and references (Ref).

Serial No.	Materials	Specific/Areal Capacitance (C_s)	Current Density (ρ_c)	Scan Rates	No. of charging & discharging cycles (C_i)	Percentage of retained capacitance at C_i (C %)	Ref
1.	$CoMoO_4$/CTAB with chitson	71 $F\ g^{-1}$	2 $mA\ cm^{-2}$		2000	81	[9]
2.	PEDOT-modified DAAQ–TFP	197 $F\ g^{-1}$		0.5 mVs^{-1}	10,000	80	[12]
3.	c–PANI	300–1100 $F\ g^{-1}$	f 5 $A\ g^{-1}$		20,000	86	[13]
4.	TpDAB	335 $F\ g^{-1}$		2 $mV\ s^{-1}$	1000	93	[24]
5.	N3-CMP-1	260 $F\ g^{-1}$	5 $A\ g^{-1}$		10,000	100	[25]

6.	PANI hydrogel	320 F g^{-1}	2 A g^{-1}		2000	93	[14]
7.	P4	315 F g^{-1}	0.5 A g^{-1}		500	79	[31]
8.	HPC-3	67.8 F g^{-1}	0.5 A g^{-1}		5000	96	[39]
9.	PD4	39 F g^{-1}		10 mVs^{-1}	500	79	[31]
10.	PANAB	133.6 Ah kg^{-1}	200 mA g^{-1}		181	96	[32]
11.	$Li_3V_2(PO_4)_3$@PEDOT	108.9 mAh g^{-1}		0.2 mVs^{-1}	500	96.6	[26]
12.	POMA	260 F g^{-1}	4.5 A g^{-1}		3000	70	[15]
13.	3D rGO/PANI	381 F g^{-1}	4.0 A g^{-1}		1000	83	[19]
14.	MnO2@PPy AFSCs	47.2 F g^{-1}	3Ag^{-1}		6000	90.3	[29]
15.	PEDOT:PSS aerogels	120 F g^{-1}	40 mA g^{-1}		1000	90	[28]
16.	RG@ (Fe2P⊂NPC)	1098 F g^{-1}	1 A g^{-1}		1000	77.9	[40]
17.	PTMA	83 m Ah g^{-1}	100 mA g^{-1}		1000	55	[33]
18.	PPy-A-4	328 F g^{-1}	1 A g^{-1}		3000	90	[34]
19.	graphene@PANI	414 F g^{-1}	0.5 A/g		6000	80.5	[16]
20.	MP-MX_2	351 F g^{-1}	0.5 A g^{-1}		1000	90.5	[41]
21.	LSG	350.66 F g^{-1}	3.84 A g^{-1}		10,000	90	[42]
22.	PEDOT:PSS/CNT	85.3 F g^{-1}	0.15 mA cm^{-2}		2000	93	[43]
23.	CNT/graphene	138 F g^{-1}	1 A g^{-1}		5000	78	[30]
24.	c-PEO-PEDOT:PSS/PEI)	2000 m Ah g^{-1}	1.0 A g^{-1}		5000	75	[27]
25.	PANI-S	184 m Ah g^{-1}	0.2 A g^{-1}		2000	70	[44]
26.	PICA wires	16.20mF cm^{-2}	0.1mA cm^{-2}		1000	93	[36]
27.	PDAQ-BC	180.5F g^{-1}	1A g^{-1}		5000	84	[37]

28.	DBQ@rGO	500 F g^{-1}	10–50A g^{-1}		10,000	90	[38]
29.	BC/PPy	1.71F cm^{-2}	0.4mA cm^{-2}		10,000	90	[35]

1.	PANi hydrogels	492 F g^{-1}	1 A g^{-1}		10,000	97.1	[22]
2.	APPH-2 electrodes	260F g^{-1}	0.5 A g^{-1}		2000	90	[20]
3.	PP60P	770.6mF cm^{-2}	2.0 A cm^{-3}		10,000	71.4	[45]
4.	rGO/CNT/PANI	116.9 F g^{-1}		1000 mV s^{-1}	10,000	82.2	[21]
5.	PPM	151.9 mF cm^{-2}	0.1 mA cm^{-2}		5,000	79.5	[23]
6.	CS:LiCO2CH3: Glycerol	77.36 F g^{-1}		10 mV s^{-1}	700	99.5	[46]
7.	Fe2O3@PPNTs-NF	712.7 F g^{-1}		2 mV s^{-1}	6000	81.4	[47]
8.	P5FIn/WO3	26.64 mF cm^{-2}		25 mV s^{-1}	5000	86	[17]
9.	CPHs	560 F g^{-1}	0.75A g^{-1}		5000	82	[48]
10.	PDA/PANI/PPy	32 F g^{-1}		10 mV s^{-1}	250	96	[2]
11.	PPy-Mo_7O_{24}	235 F g^{-1}	2 mA cm^{-2}		5000	96.4	[49]
12.	PEDOT-intercalated AVNFs	344 mAh g^{-1}	0.5 A g^{-1}		1000	94	[50]
13.	DC-TAPDA	160 mAh g^{-1}	160mAh g^{-1}		1000	67.5	[18]
14.	PEDOT:PSS/rGO	215.6 F g^{-1}	1 A g^{-1}		5000	82.1	[51]

DISCUSSION

The results presented in this study confirm the critical role of polymeric materials in enhancing the performance of advanced energy storage systems. Conducting polymers, particularly polyaniline (PANI), polypyrrole (PPy), and PEDOT, consistently exhibit high capacitance values, rapid charge–discharge behavior, and mechanical flexibility, making them highly suitable for supercapacitor and battery applications. The data extracted from the reviewed studies show capacitances ranging between 380 and 480 F g^{-1} for PANI and PPy hydrogels, with conductivities as high as 1138 S cm^{-1} for PANI/rGO composites. These findings not only surpass many conventional carbon-based materials but also demonstrate the synergistic benefits achieved when polymers are combined with nanostructured fillers such as graphene or carbon nanotubes. Importantly, the improvement in conductivity and stability directly correlates with morphological control and dopant selection, emphasizing the significance of structural engineering in conducting polymer design.

Redox-active polymers (RAPs) emerged as another promising class of materials, providing stable redox centers capable of sustaining long-term cycling.

TEMPO-based polymers such as PTMA achieved specific capacities of 77 Ah kg^{-1} with stability maintained for more than 500 cycles, while ferrocene-containing polymers demonstrated coulombic efficiencies exceeding 99.8% under elevated temperatures. These results confirm the hypothesis that introducing stable radical groups into polymer chains can enhance both capacity retention and energy efficiency. However, compared with conducting polymers, RAPs still face limitations in terms of energy density, typically lower than 100 mAh g^{-1}, suggesting that further molecular tailoring and hybridization strategies are required to reach commercial competitiveness.

Polymer electrolytes and membranes have also demonstrated substantial potential in replacing conventional liquid electrolytes and Nafion membranes. The reviewed data indicated proton conductivities of 0.03–0.173 S cm^{-1} for sulfonated polymers such as SPEEK and SPSU composites, rivaling or even surpassing Nafion under hydrated conditions. The Nafion–SPSU hybrid membranes achieved four times higher power generation at 120 °C compared to pristine Nafion, a significant milestone in polymer fuel cell research. Such advances not only improve performance but also address cost and sustainability concerns, since many sulfonated polymers can be synthesized from less expensive and more abundant precursors. Still, the mechanical stability of these membranes remains a barrier, with several reports highlighting degradation after extended operation, particularly under dry or high-temperature conditions.

Another key finding from the literature was the superior performance of polymer composites compared to pure polymers. Table data from the reviewed studies demonstrated that PANI/rGO composites retained 97% of their capacitance after 10,000 cycles, while MnO_2/PPy hybrids exhibited capacitances of 315.8 F g^{-1} with 90% retention over 6000 cycles. Similarly, nanocellulose-based polymer composites achieved energy densities of 45.7 mWh cm^{-2} with nearly 100% retention after prolonged cycling, underscoring their dual advantages of flexibility and sustainability. These outcomes validate the growing consensus in the literature that multifunctional composites, integrating polymers with carbon nanostructures or metal oxides, provide a balanced solution to address conductivity, capacitance, and cycling stability simultaneously.

Despite these advances, the analysis highlights several limitations. Conducting polymers often suffer from volumetric swelling and shrinkage during repeated doping–dedoping processes, leading to capacity fading beyond 5000 cycles in some studies. Similarly, polymer electrolytes exhibit comparatively low dielectric constants (≈3.5 for most polymers except PVDF), restricting their energy storage potential. These challenges are consistent with prior reviews that emphasize the need for advanced molecular design and nanostructuring techniques. Therefore, while polymers show undeniable promise as next-generation materials for energy storage, their full commercialization will depend on overcoming these technical barriers and achieving scalable, cost-effective production methods

6. Conclusion and Recommendations

This study reviewed and synthesized recent advancements in the use of polymeric materials for energy storage devices, focusing on batteries, supercapacitors, and fuel cells. The findings confirm that polymers, particularly conducting and redox-active types, exhibit remarkable electrochemical properties, including capacitances above 400 F g^{-1}, conductivities exceeding 1000 S cm^{-1}, coulombic efficiencies greater than 99%, and cycle stabilities reaching 10,000 cycles in optimized systems. Polymeric electrolytes such as sulfonated poly(ether ether ketone) and polysulfone-based membranes demonstrated proton conductivities comparable to or surpassing Nafion, highlighting their potential as cost-effective alternatives in fuel cell applications. Moreover, polymer composites with carbon nanostructures and metal oxides consistently outperformed pure polymers, validating the effectiveness of hybrid strategies in addressing conductivity and durability challenges.

However, several limitations remain. Conducting polymers are prone to mechanical degradation during repeated cycling, while redox-active polymers generally deliver lower energy densities than their inorganic counterparts. Similarly, polymer electrolytes, though safer than liquids, still face issues of long-term stability and limited dielectric constants.

These barriers currently restrict large-scale industrial adoption, despite significant laboratory progress.

Based on the findings, the following recommendations are proposed:

1. **Molecular Engineering:**

Future research should focus on designing polymers with improved structural stability to resist volumetric changes during cycling.

2. **Composite Development:**

Greater emphasis should be placed on multifunctional composites, particularly those integrating graphene, MXenes, or metal oxides, to enhance conductivity, energy density, and cycling performance.

3. **Green Synthesis Approaches:**

Sustainable and scalable polymer synthesis using renewable precursors and eco-friendly solvents must be prioritized to reduce costs and environmental impact.

4. **Device Integration:**

Efforts should move beyond material synthesis to full device assembly, ensuring compatibility between electrodes, electrolytes, and membranes under real-world conditions.

5. **Long-Term Testing:**

Extended testing beyond 20,000 cycles under varied environmental conditions is essential to evaluate the commercial viability of polymer-based devices.

In conclusion, polymers represent a transformative class of materials that, with continued innovation in molecular design, composite engineering, and eco-friendly processing, hold the potential to drive the next generation of sustainable, high-performance energy storage technologies

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