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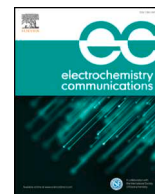
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Polymer of intrinsic microporosity (PIM) films and membranes in electrochemical energy storage and conversion: A mini-review

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ABSTRACT

Polymers of intrinsic microporosity (or PIMs) have emerged as practical film or membrane materials for a range of electrochemical technologies. Fundamentally, PIMs are based on highly rigid polymer backbone structures, which are inefficient for packing into solid films or structures. Poor packing in the solid is linked directly to (i) good solubility and processability, (ii) to glassy structures with persistent microporosity, (iii) to interesting permeation and separation properties for ions and for neutral molecular species, and (iv) to pore retention during pyrolysis. Further modification by cross-linking, introduction of charged functional groups, and hybrid material formation has been reported for applications in batteries, capacitors, fuel cells, and flow energy storage systems. This mini-review highlights recent applications suggested for PIMs in electrochemical energy systems.

1. Introduction to PIM films and membranes in electrochemical systems

A micropore is defined a pore of less than 2 nm diameter [1], which is close to the size of individual molecules. Therefore, microporous materials are able to control transport and reactivity of molecular species. Most microporous materials are insoluble (e.g. MOFs [2] or zeolites [3]) and, therefore, produce “grainy” inhomogeneous films when processed. For many application, especially those in electrochemistry, being able to coat or deposit uniform microporous films without grain boundaries is crucial. Polymers of Intrinsic Microporosity (PIMs) have emerged, based on initial work by Budd et al. [4], and triggered great interest for application as gas separation membranes [5]. However, over the past 5–7 years PIMs have also become more prominent in studies focusing on electrochemistry [6].

Initial studies focused on physical electrochemistry exploring the ability of PIM-EA-TB (PIM = polymer of intrinsic microporosity, EA = ethanoanthracene, TB = Tröger base coupling, see Fig. 1A) to accumulate water-soluble ions such as PdCl_4^{2-} at the electrode surface [7], and to suspend and immobilise water-insoluble molecular catalysts based, for example, on TEMPO derivatives [8] close to the electrode surface [9]. PIM-EA-TB is a material with typically Brunauer–Emmett–Teller surface area (S_{BET}) of $1000 \text{ m}^2 \text{ g}^{-1}$ and 1.4 nm average

pore diameter [10]. A study of the electrochemical membrane properties of PIM-EA-TB by Madrid et al. [11] suggested potential for future application of PIM materials as membranes for example in desalination [12]. Based on these early studies, it became apparent that PIMs are readily applied to electrode and catalysts surfaces [13] to provide uniform microporous coatings with beneficial effects on the electrode properties. The material PIM-1 (see Fig. 1B; apparent $S_{\text{BET}} = 700\text{--}900 \text{ m}^2 \text{ g}^{-1}$, effective pore size $< 2 \text{ nm}$ [14]) was shown to affect how gases can interact with electrode surfaces [15,16]. This gas capture effect was beneficial, for example, in the photo-electrochemical hydrogen generation connecting the semiconductor particle with the underlying electrode (Fig. 1B [17,18]). Similarly, the polymer PIM-7 was shown to affect gas evolution at the electrode surface for CO_2 evolution from formic acid [19].

For gas-evolving or gas-consuming electrode reactions, intrinsic microporosity allows the gaseous phase and the liquid electrolyte phase to coexist. But also the capture of pollutants from solution into a PIM to preferentially react on photochemically active ZnO has been proposed [20]. In a related approach, the intrinsic microporosity can be exploited by filling with anti-corrosion liquid. The resulting composite coatings were shown to provide stable films to protect aluminium alloy against corrosion [21]. Any damage to the film triggered “self-healing” due to the entrapped liquid benzotriazole seeping out.

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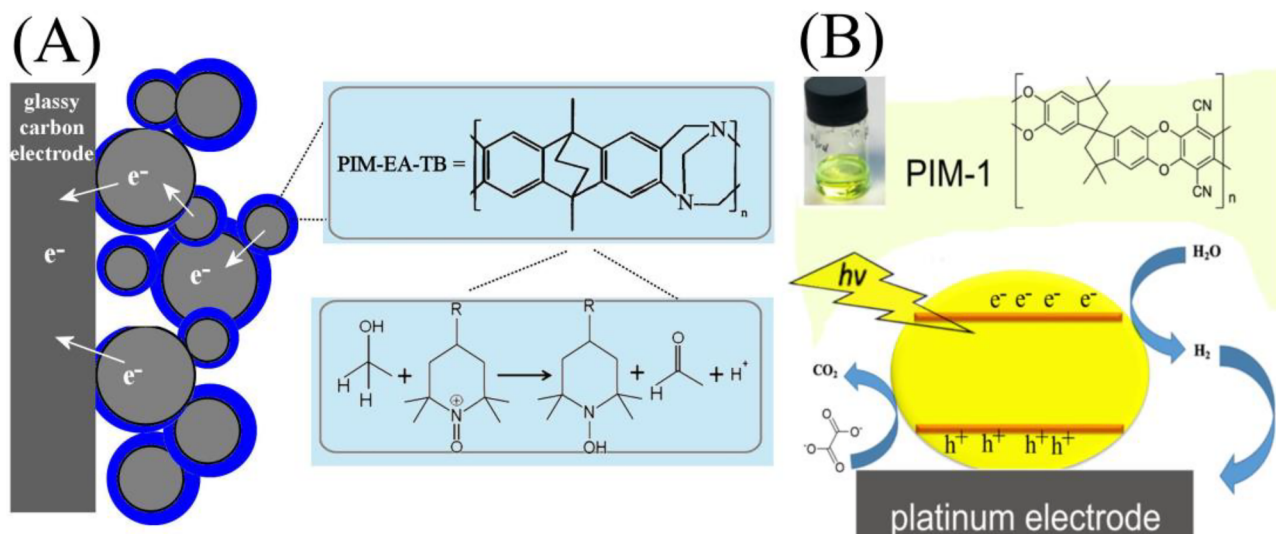


Fig. 1. (A) Molecular structure of PIM-EA-TB and application as TEMPO catalyst film on glassy carbon electrode (with permission [8]). (B) Molecular structure of PIM-1 and a photograph of a fluorescently green PIM-1 solution in chloroform. Illustration of the light-induced formation of hydrogen at semiconductor particles under PIM-1 (with permission [17]).

2. PIM films and membranes in electrochemical energy storage systems

2.1. Suppression of dendrite growth by PIM films

Lithium metal, as a common anode in batteries, offers high specific capacity (about 3860 mAh g^{-1}) [22] and low electrochemical potential (-3.04 V vs. SHE). Lithium anodes (as well as other types of metal anodes) suffer from uncontrollable dendrite or whisker growth. Device damage and loss of Coulombic efficiency may occur [23]. Even worse, fire hazards arise when dendrites create short-circuits [24]. Dendrite growth (the opposite to electro-polishing) is a surface phenomenon. Lithium ions approach the surface from solution and diffusion-migration often favours growth of sharp surface features.

As lithium is highly reactive, in most solvent systems, a solid-electrolyte-interphase (SEI [25]) forms naturally composed of polymeric organic solvent breakdown products. Moon and coworkers introduced an artificial SEI to control processes at the interface [26] based on PIM-1. Taking advantage of appropriate pore size, PIM-1 effectively prevents the direct contact of solvent molecules with the lithium metal anode. PIM-1 only allows the transport of the less solvated lithium ions with partial desolvation from propylene carbonate-solvated shells by the 0.6 nm pores [27]. This was shown to be an effective way to protect the lithium metal anode against dendrite growth.

PIM-1 was employed by Yang et al. [22] to maintain uniform flux of ions in the lithium plating/stripping process. The authors proposed a different theory of the Li^+ diffusion process. PIM-1, containing ether groups in the main chain, would trap the solvent and large anions in the network of micropores during soaking in electrolyte. Subsequently, the polymer immobilised anions and solvent facilitate the Li^+ diffusion in the channels while inhibiting side reactions. A $\text{Li@PIM-1}|\text{LiFePO}_4$ battery produced high Coulombic efficiency of about 99.7% and good cycling performance. Consistent with this, Ma and co-authors [28] suggested that in PIM-1 the Li^+ transference number increases (from 0.2 to 0.4 to > 0.7). PIM-1 may also sequesters ions from the electrolyte into its micropores whose size is on a similar scale as the Debye screening length in the bulk electrolyte resulting in a modified electrodeposition process.

PIM-DMBP-TB (see Fig. 2) has also been introduced as an interfacial layer to stabilise the interface between lithium metal anode and electrolyte [29]. PIM-DMBP-TB has high Young's modulus and is mechanically flexible enough to suppress lithium dendritic growth and to

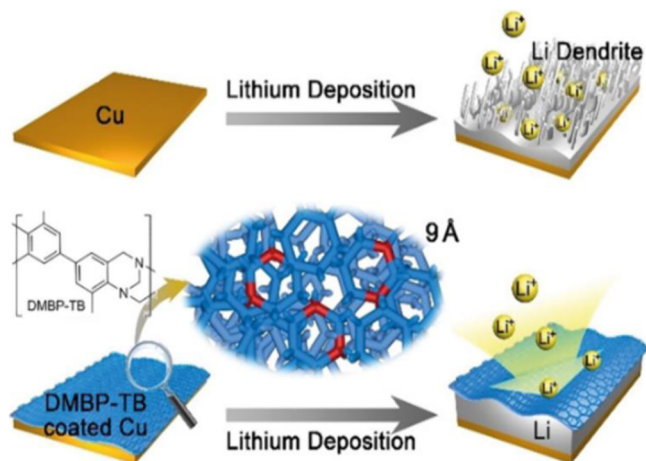


Fig. 2. Schematic illustration of Li deposition on a bare Cu electrode with Li dendrites forming or guided deposition through a PIM-DMBP-TB coated Cu electrode with suppressed Li dendrite formation (with permission [29]).

relieve the stress originating from the volume change during lithiation. In addition, the uniform well-interconnected micropores provided uniform lithium ion conduction, resulting in extended cycle lifetime of the lithium metal anode. Helms and coworkers [30] considered “explicit solvation cages” for Li^+ in PIMs and suggested that conventional upper bounds for membrane permeability and ion transport selectivity can be overcome as well as dendrite-growth suppressed with PIMs in high-voltage lithium-metal batteries.

2.2. PIM membranes as separators in batteries

In batteries, the separator between anode and cathode is an electronic insulator while providing ion transportation channels. The separator plays a critical role in determining charge-discharge rate, cycling life, and rate capacity performance. The criteria for separator include high electric insulation, mechanical rigidity, chemical stability, and most importantly, excellent thermal stability for safety. Porous polymers are the best option for producing separators. However, commercial separators including polyolefins such as polyethylene (PE) and polypropylene (PP) fail to provide sufficient ion conductivity and wettability.

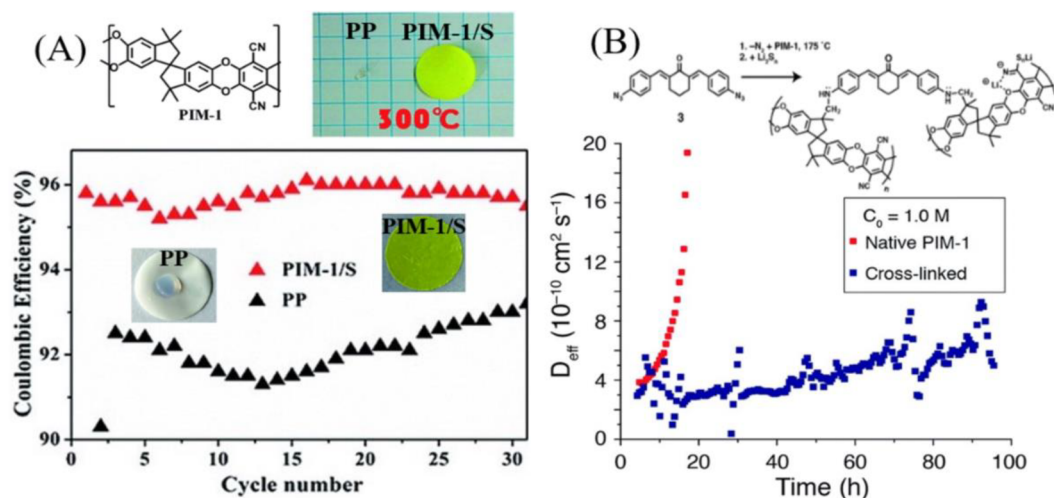


Fig. 3. (A) Photographs of PIM-1/S (yellow) and PP (white) separators after heating to 300 °C (top right). Coulombic efficiency of PIM-1/S and PP cells over 30 cycles at 1C/1C charge/discharge current rate at 60 °C (bottom). (insets: Photographs of the liquid electrolyte wetting behaviour of the two separators; with permission [31]). (B) PIM-1 cross-linking: (top) chemical cross-linking, (bottom) values of the effective diffusion coefficient (D_{eff}) for Li^+ across the native and cross-linked PIM-1 membranes as a function of time (with permission [33]).

Good Li^+ transportation properties are observed due to polar ether bonds and cyano groups in the backbone of some PIMs. PIM-1, for example, was chosen to fabricate a separator in lithium ion batteries by Tian's group [31]. As shown in Fig. 3A, PIM-1/SiO₂ (denoted as PIM-1/S) composite shows much better thermal stability at a temperature of 300 °C compared to traditional polypropylene (PP) membranes. The battery performance was evaluated by assembling lithium (anode) || PIM-1/S or PP (separator) || LiFePO₄ (cathode) coin cells. The Coulombic efficiency of the cell with PIM-1/S separator was around 96% when tested with a rate of 1C at 60 °C, which was improved compared to data for PP (about 92%). Improved battery performance was attributed to electrolyte wetting and transport in PIM-1.

For lithium-sulfur batteries, the most severe problem is the polysulfide 'shuttle effect', which can result in capacity degradation, self-discharge, and reduced charge efficiency. Simulations made by Li *et al.* suggest that the upper limit pore radius of 1.2–1.7 nm should achieve the goal of polysulfide blocking [32]. Based on size-sieving effect, PIMs were considered as the separator to suppress the polysulfide diffusion. PIM-1 [33,34] and PIM-7 [35] were adopted as separators in lithium-sulfur batteries. Although the appropriate pore size of PIM-1 enables mitigation of polysulfide shuttle problems, the nitrile groups on the polymer backbone are susceptible to attack by lithium polysulfides to form lithiated thioamides. This change in the polymer leads to chain reconfiguration by swelling with electrolyte, which reduces the ion-selective transport ability. Doris and co-workers therefore controlled swelling by cross-linking PIM-1 [33]. Fig. 3B illustrates the cross-linking reaction. The modified PIM-1 membrane maintains dramatically enhanced long-term polysulfides blocking ability with low polysulfide crossover rates sustained for > 95 h. PIM-7 also reacts with polysulfide to provide benefits as the separator in lithium-sulfur batteries. Ward *et al.* [35] proved that PIM-7 is reduced to a dilithiated state when in contact with sulfur-based reductants. The phenazine part in PIM-7 structure is a redox switchable unit and activated in situ when lithium sulfides enter the pores of the membrane. The transformation reinforces the polysulfide blocking ability while maintaining the ionic conductivity of the membrane.

PIMs have been proposed as a separator in Li/Na-H₂O₂ batteries. A PIM-1 membrane was modified with carboxyl groups by Zhao and co-workers to improve cation conduction [36]. The cyano (-CN) groups in as-synthesised PIM-1 was converted into carboxyl (-COOH) groups, followed by an ion-exchange process to obtain Li-form or Na-form of the membrane to be further applied to batteries. The resulting PIM-1-

COOLi/Na products deliver remarkable Li^+ or Na^+ conductivity in both aqueous and organic electrolytes and good solvent permeation resistance in model Li/Na-H₂O₂ batteries. The discharge performance of PIM-1-COOLi/Na separator is comparable to that of commercial inorganic lithium super-ionic conductor (LISICON).

A new type of Na-S battery system was suggested by Jeon and coworkers [37] with PIM-1 integrated into the electrode. A mixture of PIM-1 and sulfur was carbonised to provide electrically conducting microporous sulfur-containing structures. Carbonisation of PIM materials results in retention of porosity due to the rigidity of the molecular backbone [38] and therefore materials can be embedded in a one-step process giving modified porous carbons [39]. In the sulfur-cPIM-1 structure the sulfur redox system is retained and not lost during redox cycling. A room temperature sodium-sulfur (RT Na-S) battery was demonstrated with long cycling stability over 250 cycles, with a capacity of 556 mA h g⁻¹, and a coulombic efficiency of approximately 100% with physical confinement of sulfur in PIM-1.

2.3. PIM films in supercapacitors

Supercapacitors, are widely used in electric vehicles/transport, in sensors, and as backup power for computers and electronic equipment. According to energy storage mechanisms, supercapacitors are divided broadly into two general types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store electrical energy through the electric double layer, in other words, electrostatic interaction between the electrode and the electrolyte ions. Therefore, the capacitance of EDLCs is highly dependent on the surface area of the electrode material [40]. Porous carbon-based materials provide active material for EDLCs. The pore size distribution and pore volume of carbon materials determine the surface area of the electrodes available for electrolyte access, charging rate, and thus the capacitor performance. Associated with the microporous nature of PIMs, it could be a rational approach to produce porous carbon by carbonising PIMs material. PIMs retain backbone and intrinsic porosity during vacuum thermolysis and therefore generate porous carbons in a single reaction step as has been demonstrated for PIM-EA-TB [38] and for PIM-EA-TB-H₂ [41].

PIM-1 was used to fabricate flexible and freestanding carbon nanostructures by electrospinning followed by pyrolysis [42]. During carbonisation only a slight loss of apparent S_{ABET} occurred from 760 m² g⁻¹ for PIM-1 to 546 m² g⁻¹ for cPIM-1. Steam treatment increased the surface area to 1162 m² g⁻¹ to give a binder-free symmetric

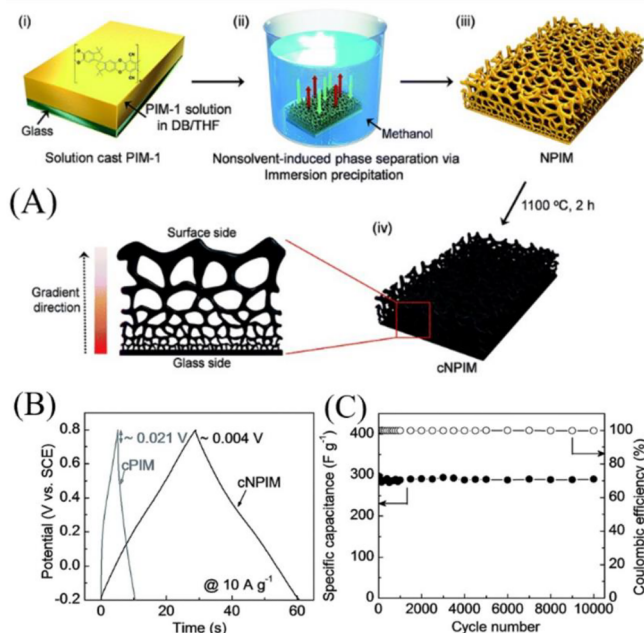


Fig. 4. (A) Schematic illustration of the fabrication of cNPIM. (B) Three-electrode GCD profiles (at a constant current of 10 A g^{-1}). (C) Long-term stabilities and coulombic efficiencies of cNPIM electrodes over 10,000 GCD cycles at a constant current of 10 A g^{-1} in a three-electrode configuration (with permission [43]).

supercapacitor with specific capacitance of 120 F g^{-1} at 10 mV s^{-1} scan rate in 1,3-ethylmethylimidazolium bis(trifluoromethanesulfonyl) imide (EMITFSI) ionic liquid electrolyte.

Jeon *et al.* developed a nonsolvent-induced phase separation routine to prepare hierarchical porous carbon structure based on PIM-1 [43]. Fig. 4A shows the steps of the fabrication process based on casting the PIM-1 solution (dissolved in mixture 1,2-dichlorobenzene and THF) on a glass slide and immersion of the nascent PIM solution in a nonsolvent (methanol). The final product with a pore size gradient was obtained after carbonisation (cNPIM). Galvanostatic charge–discharge (GCD) profiles displayed a symmetric triangular shape, and long-term cycling stability was reported.

3. PIM films and membranes in electrochemical energy conversion systems

3.1. PIMs in fuel cell systems

Electrochemical energy conversion systems (defined here in contrast to closed energy storage systems in terms of being open to fuel supply) considered here comprise both fuel cells and redox flow cells. In fuel cells, PIMs are of interest as a catalyst binder, as a component in gas diffusion electrodes, and free-standing in proton exchange membranes. PIM-1 which does not contain charged functional groups, was sulfonated to give cation conductivity and a new oxygen permeable binder for fuel cell applications [44]. Although the PIM-1 material promised 2000-times higher permeability for oxygen when compared to traditional Nafion, the sulfonation process severely degraded the properties of PIM-1. More recently, a more successful sulfonation was reported to give improved PIMs with cation conductivity through channels [45]. The material was suggested to allow transport of protons and cations through with high selectivity towards nanometer-sized redox-active molecules for operation in aqueous alkaline quinone redox flow batteries and in a hydrogen PEM fuel cell.

There are only a few studies incorporating PIM materials into electrode design. After electrospinning and pyrolysis, PIM-1 can be

employed as gas diffusion electrode in high temperature polymer electrolyte membrane fuel cells [46,47]. The pyrolysis process produces microporous carbon with good electrical conductivity. Carbon nanofibers from electrospun PIM-1 were also employed in alkaline water electrolysis with atomic layer deposition (ALD) of a $\text{NiOOH}/\text{Ni}(\text{OH})_2$ catalyst directly into the pores [48]. Pyrolysis of PIM-1 also provided effective electrodes for redox flow systems [49]. PIMs when simply coated over electrocatalytic surfaces modify or improve electrochemical reactions. The Tröger base-type PIM-EA-TB material was applied as a thin coating over Pt@Vulcan electrodes to immobilize the nanocatalysts and to suppress any colloidal degradation processes at the electrode surface. It was shown that for methanol oxidation reactions catalyst degradation was suppressed without affecting catalyst performance [50]. PIM-EA-TB was also applied to copper gas diffusion electrocatalyst to improve the ethylene production from CO_2 [51].

The key component in the fuel cell is the ion-conducting membrane and charged PIM materials could be candidates for improvements. For cation-conducting membrane materials proton mobility and ion exchange capacity (IEC) are crucial parameter and often compared to classic Nafion with proton conductivity of typically 70 mS cm^{-2} at $80 \text{ }^\circ\text{C}$ and $\text{IEC } 0.9 \text{ meq g}^{-1}$ [52] as a benchmark. PIM-1 was employed with an arylether-type polybenzimidazole (PBI) [53]. Both PIM-1 and PBI are high temperature stable polymers and phosphoric acid can be employed to create proton conducting membranes. Membranes with intrinsic “porous” structure are obtained with proton conductivity of 313 mS cm^{-1} at $200 \text{ }^\circ\text{C}$. Hydrogen fuel cells are demonstrated with a peak power density of 438 mW cm^{-2} at $160 \text{ }^\circ\text{C}$ under anhydrous conditions.

Work on the development of anion conducting polymer membranes is important due to more difficult chemical conditions in hydroxide conductors. A rigid ladder polymer based on spirobiindane was reported [54] to give free-standing membranes with trimethylammonium hydroxide groups. Hydroxide conductivities of 65 mS cm^{-1} at $80 \text{ }^\circ\text{C}$ was observed under 100% relative humidity. A comparison of PIM-like polymers with quaternised nitrogens for chloride, hydroxide, and carbonate conductivity has been reported [55]. Perhaps surprisingly, the fully molecularly rigid PIM materials performed less well when compared to molecular structures with some rotational freedom. Therefore, entirely rigid structures may be detrimental in terms of ion transport. A record hydroxide conductivity of 164.4 mS cm^{-1} at $80 \text{ }^\circ\text{C}$ was obtained in spite of a relatively a low ion-exchange capacity of 0.82 mmol g^{-1} .

A multi-cation cross-linked Tröger’s base polymer was reported [56] based on a random copolymer precursor with monomers 4,4'-diaminodiphenylmethane (DPM) and 4,4'-diamino-3,3'-dimethyl-biphenyl (DMBP) and cross-linking with dibromohexane in DMSO. A membrane was produced with good dimensional stability (20.8% swelling ratio at $60 \text{ }^\circ\text{C}$) and excellent alkaline resistance. The membrane exhibits a hydroxide conductivity of 103.9 mS cm^{-1} at $80 \text{ }^\circ\text{C}$ with an ion exchange capacity of 1.67 meq g^{-1} . Blending of PIM-1 derived materials with polysulfones was shown to give good hydroxide conductors [57] in mechanically robust membranes. A blend with 30% PIM exhibited an ion exchange capacity (IEC) of 0.77 mmol g^{-1} with high conductivity of 16.9 mS cm^{-1} at $30 \text{ }^\circ\text{C}$. The corresponding H_2/O_2 fuel cell provided a power density of 163 mW cm^{-2} at $60 \text{ }^\circ\text{C}$.

3.2. PIMs in flow cells & flow batteries

Whereas, membranes in fuel cells require high cation/anion mobility, retention of water at elevated temperature, and chemical robustness, in contrast, membranes in redox flow systems operate at lower temperature, but are required to be highly selective to avoid cross-over of species between anode and cathode compartments. PIM-1 was reported to considerably improve Li-sulfur flow batteries [32]. Poly-sulfide cross-over processes in glyme solvents were suppressed and molecular dynamic simulations were performed to analyse these pore size effects. In a further study on PIM membranes in lithium-sulfur batteries

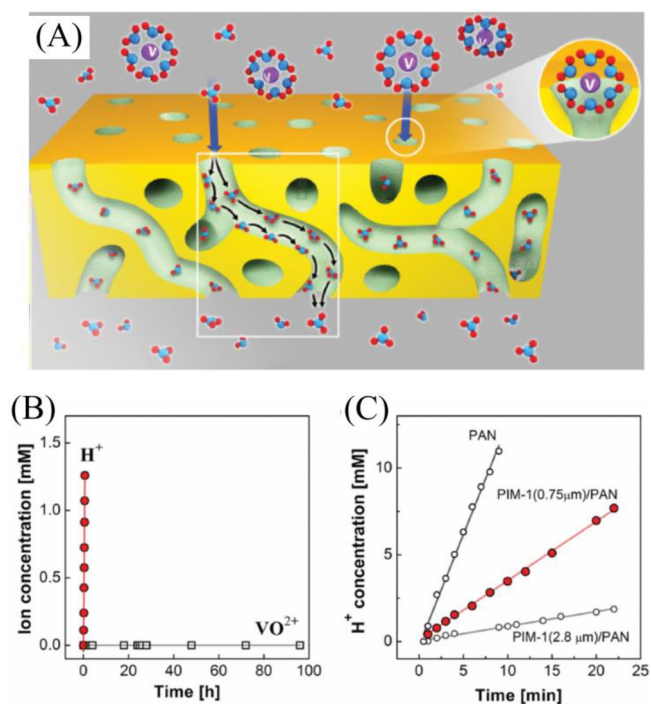


Fig. 5. (A) Schematic illustration of size exclusion effects with a PIM-1 film. (B) The H⁺/VO²⁺ selectivity of a PIM-1(0.75 μm)/PAN membrane. (C) H⁺ permeation rates when using PAN with/without PIM-1 (with permission [58]).

a markedly improved capacity, efficiency, and cycle-life were observed. In this study PIM-7 was employed and shown to react with polysulfide to alter membrane properties in situ [35].

PIM-1 was employed in vanadium redox flow systems and shown to give ultra-high proton/vanadium selectivity [58]. PIM-1 was applied in a film approx. 750 nm thin on polyacrylonitrile (see Fig. 5) to lead to extreme selectivity. Energy efficiencies of 99% and stable cycling over 100 cycles was observed.

In work on redox flow systems for grid batteries based on Zn-TEMPO-4-sulfate or Zn-K₄Fe(CN)₆, new membranes were developed derived from PIM-1 [59]. Ionizable amidoxime functionalities were obtained from nitrile groups and employed in 5 M KOH. These new materials exhibited high conductivity up to 21.5 mS cm⁻¹ and excellent selectivity for long term operation.

Size selectivity effects for ions in nanochannels can be important (in addition to ionic interactions) and were compared systematically for Tröger base PIMs and for amidoxime containing PIM-1 related materials [60]. PIMs were shown to provide easily processed ion-conductive membranes with well-defined pore architecture. Narrow molecular-sized channels with hydrophilic functionality were shown to allow high selectivity for salt (e.g. K⁺) to pass and for redox active components such as quinones, FMN, FAD, or Fe(CN)₆⁴⁻ to be excluded. Permeance measurements were reported and compared for different PIMs. These membranes enable aqueous organic flow batteries with high energy efficiency and high capacity retention. However, in this context it is interesting to add that Tröger base polymers like PIM-EA-TB also show gating behaviour with proton absorption being linked to selective Fe(CN)₆⁴⁻ accumulation [61] and therefore a simplistic size-selection rule for ion permeation may not always be suitable. In aqueous systems, a potential problem with microporous membranes occurs with some “pore-blocking” molecular species slowly poisoning the transport. This issue was investigated for PIM-1 under vanadium flow cell conditions [62]. It was concluded that this type of blocking is reversible with solvent washing routines.

Non-aqueous all-organic redox flow batteries based on solvents such as acetonitrile, propylenecarbonate or dimethoxyethane offer stable

environments for redox state switching with organic-soluble redox systems such as viologens or oligomeric redox-active organics. Celgard was compared to PIM-1 and to cross-linked PIM-1 [63] and size selection effects were clearly demonstrated. By increasing the size of the redox active species, for example employing oligomeric cyclopropenium cations, PIM-1 selectivity can also be improved and made effective for organic redox flow systems [64].

4. Conclusion and outlook

PIMs are an emerging and versatile class of molecular polymer material which offer useful micropore size, surface energy, and architecture and have proved effective membranes and coatings on electrodes. Intrinsic microporosity in films and membranes offers new solutions to problems including catalyst immobilisation and stabilisation, permeation of ions and neutrals, suppression of dendrite formation in the SEI, formation of microporous carbon and hybrid materials, and enhanced triphasic catalysis.

Based on the current rapid progress in the application of PIM materials (as well as progress in the application of other microporous materials [65–68]) in electrochemical energy storage and conversion, it seems clear that there are many more opportunities in particular in artificial SEIs for batteries, highly selective membranes for redox flow cells, modified electrocatalysts for fuel cells, and new types of microporous capacitor materials [69]. Molecular structure tuning will provide better task-specific PIM materials and work on durability and long term performance will help establishing PIMs as important engineering materials of the future.

Declaration of Competing Interest

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

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