

Perspective

Electrocatalytic Hydrogenation Using Palladium Membrane Reactors

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ABSTRACT: Hydrogenation is a crucial chemical process employed in a myriad of industries, often facilitated by metals such as Pd, Pt, and Ni as catalysts. Traditional thermocatalytic hydrogenation usually necessitates high temperature and elevated pressure, making the process energy intensive. Electrocatalytic hydrogenation offers an alternative but suffers from issues such as competing H₂ evolution, electrolyte separation, and limited solvent selection. This Perspective introduces the evolution and advantages of the electrocatalytic Pd membrane reactor (ePMR) as a solution to these challenges. ePMR utilizes a Pd membrane to physically separate the electrochemical chamber from the hydrogenation chamber, permitting the use of water as the hydrogen source and eliminating the need for H₂ gas. This setup allows for greater control over reaction conditions, such as solvent and electrolyte selection, while mitigating issues such as low Faradaic efficiency and complex product separation. Several representative hydrogenation reactions (e.g., hydrogenation of C=C, C≡C, C≡C, C≡N, and O=O bonds) achieved





via ePMR over the past 30 years were concisely discussed to highlight the unique advantages of ePMR. Promising research directions along with the advancement of ePMR for more challenging hydrogenation reactions are also proposed. Finally, we provide a prospect for future development of this distinctive hydrogenation strategy using hydrogen-permeable membrane electrodes.

KEYWORDS: Hydrogenation, Electrocatalysis, Palladium Membrane, Water, Organic Transformation

1. INTRODUCTION

Hydrogenation is an important chemical process in which hydrogen atoms are added to unsaturated bonds or replace existing functional groups, facilitating the synthesis of more valuable molecules. Accounting for approximately 20% of all chemical processes, hydrogenation is indispensable in a range of industries, from petrochemicals and pharmaceuticals to agrochemicals, fine chemicals, and dietary supplements.¹⁻²³ Extensive studies in catalysis revealed the unique activities of metals like Pd, Pt, and Ni in facilitating hydrogenation reactions.⁴ These early discoveries served as the foundation for the rapid advancement of the petrochemical industry and have significantly shaped modern catalysis theories and techniques. Notably, hydrogenation reactions are renowned for their high selectivity, ease of workup, and the potential for catalyst recovery and recycling, thereby achieving exceptional atomic efficiency.⁵ However, the traditional thermocatalytic hydrogenation is usually carried out at high temperature and elevated pressure of hydrogen (H_2) gas, resulting in significant energy and financial expenditures.

Compared to traditional thermocatalytic hydrogenation, electrocatalytic hydrogenation offers several advantages due to its elimination of the need for H_2 .^{6–78} First, it circumvents the kinetic barrier associated with the thermal splitting of H_2 , allowing for reactions to occur under ambient conditions.

Second, the issues related to the low solubility and mass transport of H_2 in reaction solutions are also avoided, as water can commonly serve as the hydrogen source. During electrocatalytic hydrogenation, protons (H^+) from water or other sources are reduced to form adsorbed hydrogen (H^*) on the cathode surface, which subsequently hydrogenates substrates present in its proximity. Concurrently, an oxidation reaction, such as water oxidation, takes place at the anode to balance the electron flow. The availability of a variety of electrocatalytic hydrogenation process facile and instantaneous. In fact, it has been demonstrated that most organic functional groups, including C=N and C=O bonds, that can be hydrogenated by thermocatalytic hydrogenated.^{9,10}

Furthermore, the compatibility of electrocatalytic hydrogenation (ECH) with electricity from renewable sources like solar and wind energy enhances its industrial viability.¹¹

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Figure 1. (a) Simplified scheme of tPMR for the hydrogenation of an organic substrate (R) using H_2 as the hydrogen source. (b) Gas-phase hydrogen permeation, where H_2 dissociates at the Pd membrane surface and the resulting hydrogen atoms permeate through the membrane. (c) Simplified scheme of ePMR for the hydrogenation of an organic substrate (R) using H^+ as the hydrogen source. (d) Electrochemical hydrogen permeation, where H^+ sourced from water is reduced to hydrogen on one side of a palladium membrane electrode and permeates it to the other side.

However, electrocatalytic hydrogenation is not without limitations. A notable drawback is the competing hydrogen evolution reaction (HER) at the cathode, which has relatively fast kinetics. To achieve significant hydrogenation rates, a highly negative potential is often required, exacerbating the HER and thereby lowering the Faradaic efficiency of the target hydrogenation reaction. Additionally, the solubility of organic substrates in protic electrolytes can be a limiting factor for large-scale applications, restricting the solvent choices. Lastly, the need for a supporting electrolyte complicates product separation and purification, making these processes energyintensive and increasing the cost of electrolyte recycling. Consequently, several promising research strategies have been explored to address these limitations of conventional electrocatalytic hydrogenation. For instance, a considerable amount of effort has been directed toward the rational design of competent catalysts with high efficiency and selectivity, with the aim of suppressing HER and other undesired side reactions.^{12,13} Additionally, incorporation of solid electrolytes into electrochemical setups and the utilization of membrane separation techniques have also been proven effective for the separation and purification of products.^{14–16}

2. PALLADIUM MEMBRANE REACTORS

In the field of catalytic membrane reactors, materials, such as Pd and palladium alloys, were initially employed. The phenomenon of hydrogen absorption by Pd was first observed by Graham in 1866.^{17,18} In the face-centered cubic lattice of palladium, its octahedral holes can accommodate hydrogen atoms up to a H/Pd ratio of approximately 0.7 when subjected to H₂ gas or a reductive potential.¹⁹ The electrocatalytic absorption of hydrogen into a Pd cathode was initially reported in 1939 and recent studies have shown that high-current electrolysis can push the H/Pd ratio above 0.9.^{20,21} While a

few other metals, such as V, Nb, Ta, and Y, can also form interstitial alloys with hydrogen, their hydrogen absorption characteristics involve multiphase transitions. These transitions result in irreversible damage to their lattice structures, rendering these materials less suitable for membrane reactor applications.²² Even though less expensive metals like Ni, Fe, and Ti also exhibit hydrogen permeability, they have much larger hydrogen transfer resistance compared to Pd.²³ In contrast, the face-centered cubic lattice of Pd is renowned for its octahedral interstitial voids, providing ample accommodation space for individual hydrogen atoms and exhibiting excellent permeability characteristics. In fact, the selective permeability of hydrogen through Pd gave rise to the concept of "membrane catalysis" in the 1960s (Figure 1a).²⁴ Palladium and its alloys were utilized in thermocatalytic Pd membrane reactors (tPMRs), which deliver high-pressure H_2 gas on one side and accommodate reactants on the opposite side. Gasphase hydrogen permeation involves the dissociation of H₂ molecules at the Pd membrane surface, allowing hydrogen atoms to permeate through the membrane (Figure 1b). These reactors are versatile, finding applications in hydrogenation, dehydrogenation, and hydroxylation reactions, as well as in the separation of H_2 from mixed gases.^{25–31} Studies have shown that hydrogen diffusing through a Pd membrane results in faster hydrogenation rates compared to scenarios where both the organic reactant and H₂ are in direct contact on the same surface of the metal catalyst.³² This enhancement in reaction kinetics is attributed to the elimination of competition for surface binding sites, as H_2 is adsorbed on the opposite side of the Pd membrane. Moreover, subsurface hydrogen is more energetic and follows different pathways during hydrogenation, affecting both the reaction rate and selectivity.^{33,34} Despite these advantages, tPMRs still require high-pressure and hightemperature conditions for H₂ gas, which substantially increase



Figure 2. Hydrogenation of (a) styrene and (b) *para*-methylstyrene in neat conditions, (c) 1-(but-3-en-2-yl)-4,5-dimethoxy-2-propoxybenzene in benzene, and (d) 1,3-butadiene in the gas phase using ePMR.

the capital investment by demanding either a nearby highpressure hydrogen source or an upstream compressor. Additionally, elevated reaction temperatures may promote undesired side reactions, particularly when dealing with complex feedstocks.^{35,36}

In 1996, Iwakura et al. introduced an electrocatalytic palladium membrane reactor (ePMR) that effectively hydrogenated styrene to ethylbenzene using water as the hydrogen source (Figure 1c).³⁷ This innovative reactor design addresses several limitations inherent in the traditional electrocatalytic hydrogenation systems. Unlike conventional setups where the hydrogen source and reactants are in the same electrochemical cell, ePMR employs a Pd membrane to serve dual roles: as a cathode for electrochemical H* generation and as a physical barrier separating the hydrogenation chamber from the electrochemical chamber. As shown in Figure 1d, hydrogen atoms are generated upon the reduction of protons on the electrochemical side of the Pd membrane, resulting in the formation of a palladium-hydrogen alloy (Pd + xH^+ + $xe^ \rightarrow$ PdH_x). Within this alloy, hydrogen permeates and subsequently engages in a reaction with an unsaturated substrate $(PdH_x + R \rightarrow PdH_{x-1} + R-H)$ situated in an adjacent compartment that is electrically isolated. ePMR's unique architecture allows for the sourcing of hydrogen from water through a Faradaic process, which contrasts with traditional thermocatalytic hydrogenation methods. Simultaneously, the hydrogenation reaction in ePMR proceeds via a non-Faradaic process, differing from standard electrocatalytic hydrogenation. Notably, there is an absence of an electrical double layer on the Pd membrane side facing the hydrogenation chamber, eliminating any influence on the hydrogenation steps. This design also liberates the choice of solvent in the hydrogenation

chamber from the constraints of protic solvents, thereby enabling higher substrate solubility. ePMR not only creates a hydrogenation environment nearly identical to those of heterogeneous thermocatalytic hydrogenation but also avoids the utilization of H_2 . Essentially, the Pd membrane acts as a "hydrogen sponge", providing a controllable flux of adsorbed hydrogen atoms for the hydrogenation reaction. This can be fine-tuned simply by adjusting the electrochemical parameters. Overall, the design of ePMR expands the range of viable solvents, electrolytes, and substrates, while lifting the limitations related to the solubility of reactants in protic electrolytes. Additionally, the use of ePMR simplifies downstream product purification and electrolyte recycling, hence offering both operational flexibility and representing a significant advancement in the field.¹⁹

3. APPLICATIONS OF ePMR

Due to the clear benefits of using permeated hydrogen atoms for hydrogenation reactions in a chamber separate from the electrochemical cell, extensive research on various organic hydrogenation reactions employing ePMR has been conducted over the past three decades. The subsequent sections aim to concisely review representative examples to emphasize the distinct advantages of ePMR over traditional thermocatalytic and electrocatalytic hydrogenation techniques.

3.1. Hydrogenation of Alkenes and Alkynes: Improved Selectivity and Rate

In the 1996 report, Iwakura and colleagues introduced an innovative hydrogenation system that utilized a Pd membrane electrode for the hydrogenation of styrene (Figure 2a).³⁷ This system employed a glass cell partitioned into two separate chambers by a Pd membrane electrode, which had a contact

area of 0.28 cm² and a thickness of 0.1 mm. Hydrogen atoms, electrochemically generated on the Pd membrane within the electrochemical compartment, permeated through the membrane to facilitate the hydrogenation of neat styrene in the outside chemical chamber. During the electrolysis process, it was observed that ethylbenzene was the exclusive product, and its production increased linearly with the electrolysis time following an induction period. The current efficiency for ethylbenzene production was very high, exceeding 93% during galvanostatic electrolysis at a current of 10 mA. In this system, the unmodified Pd membrane served a dual function: as the cathode for H* generation and as the catalyst for the hydrogenation of styrene. A postelectrolysis cyclic voltammogram of the Pd membrane electrode revealed a significant oxidation wave at approximately +0.3 V vs Hg/HgO, attributed to the oxidation of residual hydrogen atoms absorbed in the Pd membrane during electrolysis.

To enhance the hydrogenation reaction rate, researchers soon discovered that the deposition of additional Pd nanoparticles onto the hydrogenation side of the Pd membrane electrode (Pd/Pdm) significantly improved performance (Figure 2b).³⁸ This deposition was accomplished chemically by utilizing active hydrogen atoms that permeated through the Pd membrane electrode during galvanostatic electrolysis at a current density of 10 mA/cm². A 1 h electrolysis using 0.28 mM PdCl₂ as the Pd source effectively deposited Pd nanoparticles, commonly referred to as Pd black. The result was a remarkable 40-fold increase in the hydrogenation rate of 4-methylstyrene when using this palladinized Pd membrane electrode. This substantial enhancement in catalytic activity can be attributed to an increase in the active surface area and potentially the emergence of new active sites. Furthermore, nearly 100% Faradaic efficiency was achieved in the hydrogenation of 4-methylstyrene, leading to the formation of 4-ethyltoluene.

In traditional thermocatalytic hydrogenation, achieving chemoselective hydrogenation of olefinic double bonds without simultaneous hydrogenolysis of allylic and benzylic C-O linkages in alkenes with allyloxy and benzyloxy groups is notably challenging. However, active hydrogen atoms obtained in ePMR were shown to selectively hydrogenate olefinic double bonds. For instance, compound 1 in Figure 2c was selectively hydrogenated to produce the corresponding alkane with a 75% yield, albeit with a moderate Faradaic efficiency of 3.5% when the substrate concentration in benzene was 7 mM.³⁹ When the substrate concentration was increased to 350 mM, a significantly higher Faradaic efficiency of 32% was achieved. Other similar alkenes containing allyloxy and/or benzyloxy groups were also successfully hydrogenated to produce their corresponding reduced alkanes without hydrogenolysis, with yields ranging from 8% to 70%.

Interestingly, the solvent used in the hydrogenation chamber could also dramatically influence the outcome of the reaction. For example, when alkenes containing benzyl ether or benzyl ester functionalities were subjected to hydrogenation in an ePMR system, the choice of a protic solvent like methanol facilitated not only hydrogenation but also hydrogenolysis, leading to C–O bond cleavage.⁴⁰ These observations underscore the importance of solvent in influencing the surface condition and hence the activity of the Pd membrane electrode. The adsorption of solvent molecules on the surface of Pd_m is anticipated to influence the desorption and utilization of permeated hydrogen atoms, thereby affecting the overall

hydrogenation reaction. Solvent polarity also plays a role in the interaction between hydrogen and Pd, with polar solvents exhibiting stronger binding to the metal than nonpolar solvents. Solvents with weaker adsorption on Pd, such as nonpolar solvents, may improve hydrogen flux in ePMR.⁴¹ Additionally, the hydrogen bonding interaction of solvent will also impact the rate of hydrogenation.⁴² The overall selectivity of hydrogenation is consequently dictated by intricate interactions involving the substrate, solvent, catalyst, and hydrogen source.

Besides its utility in liquid-phase organic hydrogenation, ePMR is also applicable to gas-phase hydrogenation, paralleling its thermocatalytic counterparts. For example, Su et al. employed an ePMR for the selective hydrogenation of butadiene present in a mixed butene gas stream (Figure 2d).⁴³ Thermocatalytic hydrogenation usually serves to remove butadiene, which is an impurity that poisons alkene polymerization catalysts. However, the thermocatalytic method suffers from major drawbacks such as excessive hydrogen usage, low alkene selectivity, and the necessity of high operating temperatures, often reaching up to 350 °C. In contrast, utilizing a Pd membrane electrode in a gas-fed fixed-bed reactor allowed for selective butadiene hydrogenation to occur at ambient temperatures (25-30 °C). In this system, the Pd membrane also served as the catalyst, and water was used as the hydrogen source. The process exhibited excellent catalytic performance, achieving around 92% alkene selectivity and over 97% butadiene conversion, sustained over 360 h. The energy consumption for this process was remarkably low, at 0.003 Wh/mL butadiene, making it thousands of times more energy efficient than the thermocatalytic methods. Additionally, the absence of H₂ gas in the device eliminates associated safety hazards. Su et al. further optimized the system by fabricating a vertically aligned, tree-like array of Pd nanodendrites on the Pd membrane, which led to an appreciable increase in butadiene conversion. This modification emphasized the crucial role of enhanced hydrogen atomic sieving in increasing the overall catalytic efficiency.44

The promising results obtained in alkene hydrogenation using ePMRs led the Berlinguette group to undertake a systematic comparison between ePMR and conventional ECH reactors.⁴⁵ This study aimed to assess their performance in hydrogenating alkenes and alkynes under ambient conditions. Specifically, phenylacetylene served as the model substrate, and a methanol/HCl mixture functioned as the electrolyte in both reactors. Both systems employed Pd membrane electrodes decorated with Pd nanoparticles (Pd/Pdm) as the hydrogenation cathodes (Figure 3a,b). The primary distinction between the two setups lies in the orientation of the Pddecorated side of Pd/Pd_m. In the ECH reactor, this side was in contact with the electrolyte containing phenylacetylene. Conversely, in the ePMR setup, the Pd-decorated side faced the separate chemical hydrogenation chamber. Galvanostatic electrolysis was performed at currents of 20 and 50 mA over 24 h in both reactors. Independent of the applied current, ePMR displayed a substantially higher hydrogenation rate compared to the ECH reactor. For instance, after 8 h at 50 mA, ePMR achieved roughly 30% higher ethylbenzene yields. Complete conversion of phenylacetylene was obtained within 24 h using ePMR, whereas the ECH system yielded 75% conversion (Figure 3c,d). The variations in reaction rates can be attributed to the noncompetitive binding of organic reactants and hydrogen on the exposed Pd surface in ePMR. Additionally,



Figure 3. Comparison of phenylacetylene hydrogenation in a conventional electrochemical reactor (a) versus an ePMR (b), together with their corresponding ethylbenzene formation (c and d) at applied currents of 20 and 50 mA for 24 h.⁴⁵

subsurface hydrogen has been demonstrated to possess higher energy, allowing it to access different hydrogenation pathways and influence the reaction rates and selectivity of hydrogenation reactions.^{46,47} Reaction kinetic models further corroborated that ePMR significantly accelerated the hydrogenation rate, notably in the conversion of phenylacetylene to styrene and, subsequently, to ethylbenzene. Additionally, ePMR showed a considerable advantage in terms of the byproduct formation. Unlike the ECH reactor, which generated significant amounts of byproducts, such as methyl formate and formic acid, ePMR led to minimal impurity formation.

3.2. Hydrogenation of Aldehydes, Ketones, and CO₂: Impacts of Catalyst, Solvent, and Applied Current

In addition to the hydrogenation of C=C and C≡C bonds, ePMRs have also shown efficacy in the hydrogenation of carbonyl (C=O) bonds. For instance, when crotonaldehyde (1 M) was employed as the substrate, a Pd membrane electrode with additional Pd deposits (Pd/Pd black) yielded butyraldehyde exclusively, achieving a Faradaic efficiency of 58% at an electrolysis current of 10 mA (corresponding to a geometric current density of 26.3 mA/cm²). However, when Pt deposits were introduced onto the Pd/Pd black to form Pd/Pd black/Pt black, the substrate was converted to both butyraldehyde and 1-butanol. Intriguingly, when butyraldehyde was directly subjected to hydrogenation using the Pd/Pd black/Pt black electrode, 1-butanol emerged as the sole product. These outcomes suggest that Pt exhibits greater reactivity toward the hydrogenation of C=O bonds compared to Pd, which is more selective toward hydrogenating C=C double bonds.⁴⁸ This conclusion aligns with the findings from Mishima et al., who performed selective hydrogenation using a Pd/Pd black membrane electrode on substrates such as benzalacetone and benzalacetophenone. While the olefinic C=C double bonds in these compounds were successfully hydrogenated, the ketone functional groups remained intact. This led to the formation of benzylacetone and benzylacetophenone, respectively, thereby underscoring the selective nature of the catalyst.⁴

A comprehensive investigation assessing the efficacy of various secondary metal catalysts coated on Pd membrane



Figure 4. Impacts of catalyst (a), solvent (b), and applied current (c) for hydrogenation using ePMR.



Figure 5. (a and b) Time-dependent product conversion for (a) acetophenone and (b) styrene on different MPd/Pd_m membrane electrodes in ePMR.⁵⁰ (c) Product selectivity of furfural hydrogenation to furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), and any other products after 2 h electrolysis at 150 mA using ePMR.⁵¹

 (MPd/Pd_m) electrodes for the hydrogenation of C=C and C=O bonds was reported recently.⁵⁰ Owing to the unique attributes of ePMR, steps such as H₂ adsorption and activation to form active hydrogen species (H*) are eliminated, enabling a direct evaluation of the intrinsic hydrogenation activity of each secondary metal catalyst. As illustrated in Figure 4a, acetophenone and styrene were selected as representative ketone and alkene substrates, respectively. It was observed that the hydrogenation reactions in the ePMR system were primarily catalyzed by secondary metal coatings rather than the underlying Pd membrane electrode. Additionally, the secondary metal coating enhanced the rate of hydrogen permeation through the Pd membrane from the electrochemical chamber. Notably, these permeation rates were found to correlate with the M/H binding energy of the coated metal catalysts. Sequential hydrogenation experiments revealed that Pt exhibited the highest activity for C=O hydrogenation, followed by Au, Ir, and Pd (Figure 5a). Conversely, the relative activity for C=C hydrogenation was observed to follow the sequence Pd > Ir > Pt > Au (Figure 5b). Intriguingly, while Au is generally not considered an effective hydrogenation catalyst in conventional thermocatalytic or electrochemical methods, it demonstrated significant efficacy for both ketone and alkene hydrogenation in the ePMR system, likely because it bypasses the need for H₂ activation or proton reduction. A further noteworthy observation was that the rate of C=O bond hydrogenation in ePMR was accelerated in polar protic solvents, although the hydrogen flux remained constant. This behavior contrasts with thermocatalytic hydrogenation, where the reaction rate is substantially influenced by the solubility of H₂ in the reaction medium.

In a study examining the solvent impact, Berlinguette and colleagues employed an ePMR flow cell to scrutinize how different solvents influence both the selectivity and hydrogenation rates of furfural, a key biomass-derived platform chemical.⁵¹ Figure 5c outlines the potential hydrogenation products of furfural, including furfuryl alcohol and tetrahydrofurfuryl alcohol. The results indicated that the most favorable reaction rate and selectivity were achieved using a bulky and weakly nucleophilic solvent such as t-butanol (Figures 4b and 5c). Highly nucleophilic solvents such as ethanol and methanol were found to readily react with furfural, leading to the undesirable formation of acetal byproducts. Conversely, nonbulky weakly nucleophilic solvents like nbutanol and isopropyl alcohol were observed to react with the hydrogenation products. In stark contrast, the use of *t*-butanol as a solvent yielded no detectable byproducts. This outcome was ascribed to the steric hindrance imparted by *t*-butanol,

which effectively suppressed the undesired reaction pathways. This research underscores the pivotal role of solvent selection in optimizing furfural hydrogenation. The flexibility of ePMR allowed for real-time fine-tuning of product selectivity by varying the solvent composition, without the need for any hardware modifications to the system. Notably, the ePMR system was successful in converting furfural to furfuryl alcohol and tetrahydrofurfuryl alcohol with selectivities of 84% and 98%, respectively.

In a subsequent study, the Berlinguette group delved deeper into the influence of applied current on furfural hydrogenation via ePMR.⁵² They discovered that at elevated current densities exceeding 175 mA/cm^2 , 2-methyltetrahydrofuran becomes the primary product. Conversely, at lower current densities below 100 mA/cm², the formation of tetrahydrofurfuryl alcohol is favored (Figure 4c). This divergence in product distribution is attributable to an increased effective hydrogen "pressure" (or fugacity) within the membrane reactor under higher current conditions. The increased hydrogen fugacity alters the adsorption orientation of furfural on the Pd catalyst surface. Specifically, increased hydrogen coverage on the catalyst promotes hydrogenation of the C=O group in furfural. Given that tetrahydrofurfuryl alcohol remains inert under such ePMR conditions, the data suggest that the formation of 2methyltetrahydrofuran requires an initial cleavage of furfural's alcohol group prior to the hydrogenation of its C=C double bonds.

Beyond the hydrogenation of organic functional groups with C=O bonds, the hydrogenation of CO_2 holds considerable importance, which offers a promising pathway to address the environmental and energy-related issues associated with CO2 emissions. Considerable efforts and research endeavors are directed toward the conversion of CO₂ through hydrogenation into diverse, value-added hydrocarbons.53,54 However, the thermal stability of CO₂ poses a substantial challenge for its hydrogenation. Iwakura et al. tackled this challenge by utilizing a Pd membrane electrode (with contact area of 0.28 cm² and thickness of 50 μ m) coated with Pd catalysts in an ePMR setup (Figure 6a).⁵⁵ Prior to CO_2 reduction, the substrate side of the Pd membrane was chemically palladized using atomic hydrogen generated from galvanostatic electrolysis at current densities of either 10 or 30 mA/cm² for 1 h. They observed a correlation between increased formic acid production and the amount of deposited Pd black, suggesting an increased catalytic activity for CO₂ reduction. However, the study also noted a decline in the Faradaic efficiency for formic acid production from approximately 75% to less than 35% over a 24-h reaction period. Concurrently, there was an increase in the H_2 evolution



Figure 6. Schematics of hydrogenation of CO_2 (a), CH_3CN (b), N_2 (c), and O_2 (d) using ePMR under different conditions.

in the electrochemical compartment. This decrease in efficiency was attributed to the inhibited permeation of atomic hydrogen, likely due to the poisoning of the Pd membrane by formic acid or other adsorbed intermediates. Despite these challenges, one notable advantage of the ePMR system was the use of atomic hydrogen as both the proton source and reducing agent. This eliminated the need for dissolution of CO_2 in a solvent, enabling direct utilization of atmospheric CO_2 in the hydrogenation chamber.

3.3. Hydrogenation of Nitrates, Nitriles, and N₂

Water pollution due to nitrates presents a critical environmental concern, prompting various remediation techniques such as biological denitrification and electrocatalytic reduction of nitrates to benign N₂.^{56–58} However, both approaches have their inherent limitations. For instance, the biological denitrification method exhibits slow reaction rates, requiring stringent control to maintain anaerobic bacteria and necessitating a large reactor size. On the other hand, the electrocatalytic nitrate reduction typically occurs at a more negative potential than HER, leading to intense competition with H₂ evolution at comparable current densities. Additionally, the reduction process requires the addition of inorganic salts as supporting electrolytes to address the conductivity issues. The utilization of ePMR provides an effective solution to addressing such challenges. An ePMR system equipped with Pd-Au membrane electrodes (with projected area of 2 cm², thickness of 50 μ m, and a Pd/Au atomic ratio of 4:1) was shown to effectively hydrogenate nitrates (HNO₃ and NaNO₃) to N2 with high selectivity.59 The catalytic performance was further optimized through chemical plating of Pd black (2–20 mg/cm^2) followed by the deposition of cocatalysts Cu or Sn $(0.1-1 \text{ mg/cm}^2)$ onto the membrane electrode. The modified Cu/Sn-decorated ePMR system demonstrated remarkable catalytic activity and stability, maintaining effective reduction of nitrate to N₂ for at least 200 days. Notably, the Sn cocatalyst exhibited superior stability compared to Cu, likely due to the formation of a protective SnO_2 layer during the reaction.

Given the industrial overproduction of acetonitrile, its further valorization is of great interest. A significant challenge in the electrochemical reduction of acetonitrile is how to achieve a high selectivity for a specific product while minimizing the competing HER with a small overpotential requirement. Kornienko et al. recently employed ePMR to successfully convert acetonitrile to acetaldehyde and ammonia under ambient conditions, achieving a Faradaic efficiency of up to 60% for NH₃ production at an applied potential of -0.5 V vs Ag/AgCl.⁶⁰ Their system consistently produced NH₃ for over 80 h at -0.6 V vs Ag/AgCl with no significant changes observed in the appearance of the Pd surface. To investigate the reaction mechanism, a specialized infrared spectroelectrochemical cell was used, revealing that the reaction followed an imine hydrolysis pathway. As illustrated in Figure 6b, protons from a H₂SO₄ electrolyte were reduced and permeated through the Pd membrane electrode, enabling acetonitrile hydrogenation in the outside chamber. It was postulated that both the initial adsorption and hydrogenation of acetonitrile, as well as imine hydrolysis, occurred rapidly. However, the hydrogenation of adsorbed NH_x species on the Pd surface was identified as the rate-limiting step. The ePMR system was also applied successfully to other nitrile substrates, such as propionitrile, benzonitrile, isobutyronitrile, and acrylonitrile, with Faradaic efficiencies ranging between 12% and 21%. Although the observed maximum current density and Faradaic efficiency for NH₃ production were moderate compared to those in reported electrochemical studies, this pioneering work opens the door to ePMR-based nitrile conversion. It underscores the need for the development of more competent catalysts and system designs to facilitate this promising chemical transformation.

The conversion of N₂ to NH₃ is crucial for addressing agricultural needs, given that N₂ is abundant in the atmosphere and NH₃ serves as a key precursor for fertilizers. Although the Haber-Bosch process has traditionally been used to produce NH₃, its high energy requirements have sparked interest in more efficient methods, such as electrocatalysis.⁶¹⁻⁶³ Machida et al. demonstrated that ePMR could be used to facilitate N₂ to NH₃ conversion at temperatures between 100 and 150 °C, significantly lower than conventional thermocatalytic methods.⁶⁴ As depicted in Figure 6c, a Pd–Ag alloy tube (Pd: 75 at %; reaction area: ~7 cm²; thickness: 100 μ m) served as the cathode and was coated with a chemically deposited Ru catalyst. Operating at a hydrogen permeation rate of 0.4 mL/ min and a N₂ flow rate of 40 mL/min, NH₃ was detected in the hydrogenation chamber. The amount of NH₃ produced varied between 150 and 2000 μ mol/g, depending on the electrolysis duration. However, rapid degradation of the Ru catalyst was observed, which was attributed to catalyst aggregation. While coating the Ru catalyst with a porous Al₂O₃ layer mitigated this degradation, it also hindered the reaction rate, likely by blocking some active sites. It awaits further advancement in this direction to realize more effective NH₃ production from N₂ using ePMR, ideally under ambient conditions.

3.4. Hydrogenation of O₂ to Produce H₂O₂

Hydrogen peroxide (H_2O_2) serves as an ecofriendly oxidant with diverse applications. Nonetheless, its conventional industrial synthesis through the Riedl–Pfleiderer process is both energy- and carbon-intensive, contributing over 2.8 million tons of CO₂ emissions annually. Recent advances in electrochemical synthesis offer a promising alternative.^{65–67} In



Figure 7. (a) Selective hydrogenation of benzaldehyde catalyzed by Pd nanocubes on Pd/Pd_m leads to different products depending on the active sites (e.g., face sites versus edge sites).⁷⁵ (b) Integration of PtPd/Pd_m with enzymes enables the asymmetric hydrogenation of biologically relevant substrates.¹⁰⁸

this context, it has been demonstrated that the direct hydrogenation of O_2 to produce H_2O_2 is feasible using hydrogen atoms permeated through a Pd membrane electrode (Figure 6d).⁶⁸ The role of metal cocatalysts was identified as pivotal in this process. While H₂O₂ formation was observed using either pristine or Pd nanoparticle-coated membrane electrodes, rapid H_2O_2 decomposition also occurred. The application of a AuPd alloy layer (~10 nm) on the Pd membrane electrode effectively inhibited the cleavage of the O-O bond in H₂O₂, thereby significantly enhancing its production. Methanol was also found to enhance H₂O₂ production by stabilizing the intermediates. Using an Au₁₂Pd-coated Pd membrane electrode in a methanol/water mixture (v/v: 7/3), the concentration of H_2O_2 generated reached up to 443 mg/L. However, this process exhibited low Faradaic efficiency. When the applied current density increased from 10 to 100 mA/cm², Faradaic efficiency declined from 9.6% to 1.8%, indicating significant coproduction of H_2 and other byproducts. Additionally, direct O2 feed to the reactor could pose safety risks due to the potential mixture of residual O₂ with coproduced H₂. Therefore, optimization in terms of efficiency and safety remains a crucial aspect for further development.

3.5. Hydrodehalogenation of Contaminants

While the applications discussed thus far focus on the hydrogenation of unsaturated chemical bonds, ePMR technology is also versatile enough to facilitate hydrodehalogenation reactions, notably in the context of environmental remediation. For example, Iwakura and colleagues have demonstrated that palladized ion-exchange membranes, such as Nafion, are effective for the hydrodechlorination of 4-chlorotoluene, yielding toluene as the sole product.^{69,70} Regardless of whether cationic or anionic exchange membranes were used, electroless plating and electroplating treatments with Pd black resulted in an ePMR system that achieved remarkable Faradaic efficiency, nearly 90%, for the targeted dechlorination reaction when conducted in methanol. Expanding on this, Xu and Liu et al. developed a Rh nanoparticle-modified ePMR to address oxidized contaminants in both drinking water and industrial wastewater.⁷¹ Due to the limitations of Pd in further hydrogenating specific intermediates, Rh cocatalysts were introduced onto the Pd membrane electrode to improve system performance. The Rh cocatalysts not only increased the adsorption of pollutants but also facilitated the complete

hydrogenation of *in situ* generated intermediates. Consequently, the Rh-modified ePMR was capable of electrochemically hydrogenating a wide array of oxidized contaminants, such as trichloroacetic acid, tribromoacetic acid, and 2,4,6-trichlorophenol, achieving conversion rates of \geq 99% and yields of \geq 95% at a modest applied voltage of 1.4 V.

4. FUTURE PROSPECTS OF ePMR TECHNOLOGY

As ePMR technology continues to make strides in a range of hydrogenation applications, several promising avenues require further exploration to unlock its potential. Hereby, we highlight several future objectives in advancing the application of ePMR in various hydrogenation reactions.

4.1. Develop Competent Catalysts to Enhance Hydrogenation Efficiency and Selectivity

It is evident from the preceding discussions that catalyst plays a pivotal role in the efficacy of hydrogenation reactions in ePMR. Various cocatalysts have been employed to enhance the kinetics and selectivity of these reactions. For example, the hydrogenation side of Pd_m can be modified with coatings of Pd black, Pt, or Au. This modification significantly boosts the hydrogenation rates of unsaturated organic compounds, such as 4-methylstyrene and amaranth, by expanding the reaction zone and introducing new active sites.^{72,73} Conversely, no detectable hydrogenation products were observed when Cu or Zn were deposited onto Pd_m . This lack of activity was attributed to the weak catalytic properties of both Cu and Zn for the hydrogenation actually inhibited hydrogen diffusion through Pd_m .⁷⁴

Leveraging the benefits of ambient operating conditions and the elimination of the need for H_2 in ePMR-facilitated hydrogenation allows for precise catalytic investigations using catalysts with a well-defined morphology. In thermocatalytic hydrogenation that uses H_2 , substrate adsorption, activation of H_2 , and structural reorganization at elevated temperatures introduce complexities that have left the field without a consensus on the reaction mechanisms. Many of these complexities can be avoided when utilizing ePMR. For example, when benzaldehyde served as the model substrate, two potential products could form: benzyl alcohol through hydrogenation and toluene via hydrodeoxygenation. Employing well-defined Pd nanocubes as hydrogenation catalysts on Pd_m in an ePMR system allowed for a nuanced understanding of hydrogenation chemistry.⁷⁵ Specifically, the face sites of the Pd nanocubes exhibited first-order kinetics in the production of benzyl alcohol, whereas the edge sites demonstrated zeroorder kinetics for the formation of toluene (Figure 7a). When the active sites were titrated with organic ligands such as ethylenediamine, which preferentially bind to edge sites, there was a notable reduction in the production of toluene. This indicates that nanoparticles with a high density of edge sites could be advantageous for hydrodeoxygenation reactions.

Since the electrochemical side of a Pd_m electrode in ePMR typically employs a smooth Pd surface, catalysts are decorated on its hydrogenation side, which is crucial for improving the efficiency and scope of hydrogenation reactions. It is anticipated that modifying the composition, size, and morphology of those catalysts on Pd_m can significantly impact the activity and selectivity for target hydrogenation reactions. In addition, anchoring molecular catalysts or employing hydride transfer mediators will greatly expand the reaction scope.

4.2. Expand Reaction Scope to Include Asymmetric Hydrogenation

Among various hydrogenation reactions, asymmetric hydrogenation presents a unique set of challenges.^{76,77} The enantioselectivity typically does not stem from the target molecule itself, but rather requires the use of chiral catalysts to achieve enantiomeric excess. This chiral information, embedded within the designed catalyst, is transferred to the substrate, mimicking the enzymatic processes in nature. Although significant advancements have been made in homogeneous asymmetric hydrogenation over the years,77-99 progress in heterogeneous asymmetric hydrogenation has been comparatively slow. 100-103 An early example was reported by Fujii et al. in 1956, where Pd deposited on silk fibroin fiber acted as a catalyst for asymmetric hydrogenation.¹⁰⁴ The source of chirality was attributed to the asymmetric structure of enzyme proteins in silk fibroin. However, electrocatalytic hydrogenation has not yet reached the level of success seen in thermocatalytic hydrogenation for producing enantiomerically pure products. For example, it was hoped that electrocatalytic hydrogenation, conducted under milder conditions, might outperform thermocatalytic methods when the cathode was modified with a chiral adsorbent. However, these hopes were not realized in the hydrogenation of prochiral ketones¹⁰⁵ or methyl acetoacetate¹⁰⁶ on Raney Ni modified with optically pure tartaric acid, nor in the hydrogenation of ethyl pyruvate on Pd/C modified with cinchonine.¹⁰⁷ Several factors may explain this limited success in achieving a high enantiomeric excess through electrocatalytic hydrogenation. For instance, if electrohydrogenation dominates, then the protonation step might not occur on the cathode surface, rendering chiral modifiers ineffective. Although chiral modifiers are thought to play a significant role in the electrocatalytic hydrogenation pathway, the dynamic electrical double layer (EDL) on the cathode surface can also influence the hydrogenation steps. The presence of this EDL represents a fundamental difference between electrocatalytic and thermocatalytic hydrogenation, complicating the direct translation of successful strategies from thermocatalytic hydrogenation to electrocatalytic hydrogenation for achieving high enantioselectivity.

As alluded to previously, hydrogenation in ePMR occurs on the reverse side of Pd_m , isolated from the electrolyte solution. This environment closely mirrors that of thermocatalytic

hydrogenation but eliminates the need for external H_2 gas. Consequently, it is reasonable to hypothesize that strategies successfully applied in thermocatalytic asymmetric hydrogenation could be effectively adapted for use in ePMR. Given this context, it is anticipated that future research will focus on implementing asymmetric hydrogenation via ePMR by leveraging well-established methodologies from both homogeneous and heterogeneous thermocatalytic asymmetric hydrogenation systems.

Building on the capability of enzymes to facilitate asymmetric transformations via naturally evolved cofactors, there is growing interest in incorporating biocatalytic hydrogenation within ePMR systems to achieve enantioselective outcomes. Recent research has already shown the feasibility of asymmetric hydrogenation of aldehydes and ketones, as well as the reductive amination to produce chiral amino acids.¹⁰⁸ As depicted in Figure 7b, the interaction between surface hydrogen and water on Pd_m facilitates heterolytic cleavage of the Pd-H bond. This process generates H_3O^+ ions, transfers an electron back to the Pt-coated Pd_m, and ultimately results in the formation of a hydride ion (H^{-}) . This hydride ion subsequently reduces NAD⁺ (nicotinamide adenine dinucleotide) to form NADH, a ubiquitous cofactor involved in various enzymatic hydrogenation reactions. The unique structural design of ePMR provides an advantage in terms of enhanced enzyme stability as compared to traditional electrochemical approaches for NADH regeneration. While this hybrid electro/ biocatalytic system shows immense promise for achieving asymmetric hydrogenation, it should be noted that the Faradaic efficiency reported in the study is relatively low, ranging from approximately 1% to 16%. Nevertheless, the incorporation of chiral molecular catalysts and/or modifiers in ePMR for asymmetric hydrogenation has not been reported yet, which awaits further exploration. Based on their similarities, it is reasonable to assume that strategies successful in thermocatalytic asymmetric hydrogenation can effectively be applied to ePMR. Therefore, future research is expected to focus on implementing asymmetric hydrogenation in ePMR taking advantage of those mature strategies reported for both homogeneous and heterogeneous thermocatalytic hydrogenation systems.

4.3. Integrate Hydrogenation Reactions with Value-Added Oxidation Reactions

Analogous to all electrochemical reactions, an oxidation process, such as water oxidation, is necessary at the counter electrode to balance the overall electron flow in ePMR. Given that water oxidation demands a high voltage input and yields a low-value product (O_2) , there is a growing interest in developing paired electrolysis, wherein an organic oxidation reaction at the anode is coupled with the production of hydrogen atoms (H*) at Pdm in ePMR.¹⁰⁹ For example, as depicted in Figure 8a, the paired electrolysis system combines the oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde at the anode with proton reduction at the Pd_m cathode. The generated H* atoms permeate through Pd_m to participate in the hydrogenation of 1-hexyne. This synergistic arrangement circumvents the need for less efficient water oxidation while concurrently reducing the voltage input required, thus enhancing both the energy efficiency and the economic viability of the process.

In earlier research using ePMRs, hydrogenation was typically confined to chemical cells positioned outside of the cathodic



Figure 8. (a) Paired electrolysis consists of 1-hexyne hydrogenation at the Pd/Pd_m cathode membrane and alcohol oxidation at the anode.¹⁴¹ (b) Dual hydrogenation of maleic acid taking advantage of the low-potential oxidation of aldehyde to formate at the Pd/Pd_m anode membrane coupled with water reduction at the Pd/Pd_m cathode membrane.¹⁴²

Pd_m. A recent innovation by Sun et al. has expanded this framework by employing Pd_m as both anode and cathode, enabling concurrent hydrogenation processes at both electrodes.¹¹⁰ This dual-hydrogenation system not only doubles the product yield but also enhances the overall reaction efficiency. In this novel design, H* are generated at the Pd_m cathode through water reduction, similar to conventional ePMR systems. Uniquely, the anode facilitates the low-potential oxidation of formaldehyde to formate, thereby also generating H^\ast at the Pd_m anode. These H^\ast atoms can then permeate through the membrane electrode to catalyze hydrogenation reactions in a separate chemical chamber situated outside the anode compartment. Despite the dissimilar electrochemical processes at the anode and cathode, both contribute to the generation of H*, effectively doubling the Faradaic efficiency. As demonstrated in Figure 8b, maleic acid served as the substrate and was successfully hydrogenated to succinic acid in both external chambers adjacent to the Pd_m electrodes. Remarkably, the observed Faradaic efficiency for the conversion of maleic acid to succinic acid reached 184% at an applied current of 10 mA. Concurrently, the cell voltage was reduced by over 1 V in comparison to that of traditional singleside hydrogenation systems that require water oxidation at the anode. This innovative approach offers a promising avenue for more efficient and economically viable hydrogenation processes.

4.4. Perform Deuteration Using D_2O as the Deuterium Source

Deuterium, a stable isotope of hydrogen, is also capable of permeating through Pd_m . The substitution of hydrogen atoms with deuterium atoms—known as deuteration—provides unique molecular properties that are invaluable in the arenas

of drug discovery, development, and optimization.¹¹¹ Specifically, deuterium substitution at targeted sites within a drug molecule can modulate its metabolic pathways, resulting in enhanced drug stability, extended half-life, and reduced clearance rates.¹¹² Therefore, the development of new deuteration methods holds significant importance in the fields of life sciences and medicinal chemistry.¹¹³⁻¹¹⁵ The US FDA's approval of deutetrabenazine in 2017 marked a milestone in the development of deuterated pharmaceuticals.¹¹⁶ Despite its promising applications, deuteration in pharmaceutical research is not without challenges, especially in the development of effective synthetic methodologies for selective deuteration across diverse organic substrates.¹¹⁷ For example, direct H/D or X/D exchange techniques—substituting hydrogen or other atoms (e.g., halogens) with deuterium-often utilize D2 or deuterated reagents (e.g., NaOD, NaBD₄, LiAlD₄, LiD),¹¹⁸⁻¹²⁶ stoichiometric additives,¹²⁷ or specialized catalysts.¹²⁸⁻¹³² These methods tend to be imprecise, generally resulting in overdeuteration due to difficulties in controlling selectivity. Enzymatic deuteration offers an alternative approach by using D_2O as the deuterium source. However, this method requires specific enzymes with the ability to incorporate deuterium (e.g., alcohol dehydrogenases and amine oxidases).^{133–139} The utility of enzymatic deuteration is constrained by the limited availability of enzymes that possess the desired substrate specificity, thereby narrowing the scope of substrates that can be effectively deuterated.

The modular nature of electrolyzers, combined with the nearly endless opportunities for tuning electrochemical parameters and selecting electrocatalysts, makes the electricity-driven deuteration of pharmaceutical compounds an attractive avenue for scalable operations. Indeed, an increasing number of electrocatalytic systems have been reported for various deuteration reactions.^{140,141} In contrast to traditional electrocatalytic deuteration, where reactions occur at the cathode and the substrate and product reside in the electrolyte, the ePMR technology spatially isolates the target deuteration reactions from the electrochemical cell and, consequently, the electrolyte. Electricity-driven deuteration using ePMR offers several advantages over the thermochemical methods. First, it obviates the need for D_2 or other costly deuterium reagents by using D_2O in the supporting electrolyte as the deuterium source. This approach effectively circumvents the kinetic barriers associated with the thermal splitting of D₂. Second, the challenges posed by the low solubility and mass transport of D_2 in reaction solutions are entirely avoided, allowing for operations under ambient conditions. Regardless of the underlying deuteration mechanism, ePMR is versatile enough to deuterate most organic functional groups-including but not limited to C=C, C=O, and C=N bonds-that can be thermochemically deuterated by using D2. This method offers multiple benefits, such as broad applicability across diverse unsaturated bonds, efficient deuterium incorporation, and high site selectivity.¹⁴² Looking forward, research efforts should concentrate on the identification and development of effective catalysts for use on the deuteration side of Pdm. These would enable the deuteration of saturated bonds, facilitating transformations from C-X to C-D bonds, thus broadening the scope and utility of the ePMR-enabled deuteration approach.

4.5. Conduct In Situ Spectroscopic and Computational Studies for Mechanistic Investigation

Although ePMR has been reported for hydrogenation reactions for nearly three decades, there remains a significant shortfall in the literature regarding comprehensive mechanistic studies. This gap can be addressed by employing advanced in situ spectroscopic techniques. Infrared and Raman spectroscopies, for instance, are instrumental in identifying vibrational signatures of intermediates, thereby elucidating the nuances of H* atom migration and utilization. X-ray diffraction offers structural insights into the catalyst during reaction cycles, highlighting changes that could impact its efficiency and selectivity. Meanwhile, X-ray absorption spectroscopy, including both the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), plays a crucial role in determining the electronic and coordination environment of the catalytic sites, particularly under operational conditions. These spectroscopic methods are pivotal not only in tracking the dynamics of hydrogen absorption, migration, and utilization but also in dissecting the reaction kinetics and identifying transient intermediates that are often missed in conventional studies. By focusing on the interaction dynamics between hydrogen/proton/hydride species and surface-adsorbed substrates/intermediates/products, these techniques can unravel the complex interplay of various experimental factors, such as voltage, current, solvent, and pH. In addition, integrating theoretical calculations, like density functional theory (DFT), alongside these experimental techniques, can provide a multifaceted understanding of the reaction mechanisms. DFT, in particular, can predict electronic structures and potential reaction pathways, serving as a complementary tool to experimental observations. Such a holistic approach, combining advanced spectroscopic analysis with theoretical insights, is invaluable for deepening our understanding of hydrogenation processes in ePMR. This comprehensive investigation will not only aid in elucidating the fundamental mechanisms at play but also drive forward the development of more efficient catalysts and optimized reaction conditions in the field of hydrogenation.

4.6. Develop Cost-Effective and Robust Hydrogen Permeable Membrane Electrodes

The high cost of Pd may raise concerns about the broad applicability of the ePMR for large-scale hydrogenation processes. However, alternatives to pure Pd metal electrodes are available, requiring significantly less Pd, thereby reducing costs. One such approach is alloying Pd with Ag, a strategy that not only decreases the overall cost of the membrane electrode but also addresses the issue of hydrogen embrittlement.^{29,143} Specifically, a Pd/Ag alloy membrane with an atomic ratio of 77/23 has demonstrated both robust chemical stability and high hydrogen permeability when employed in ePMR systems.^{144,145} This membrane has proven to be effective in catalyzing the hydrogenation of diphenoquinone to biphenol. Furthermore, surface modification of this Pd/Ag membrane with platinum-alumina (Pt/Al_2O_3) enhances the hydrogenation of toluene to methylcyclohexane, illustrating the versatility and potential cost-efficiency of such alloy-based systems in ePMR applications.

In addition to alloying strategies, other techniques, such as electroless plating and electroplating, have been utilized to reduce the amount of Pd required. By depositing Pd black onto cationic or anionic exchange membranes, the amount of Pd

used can be as little as one-eighth of that required for a full Pd_m. These palladized ion-exchange membranes have demonstrated effectiveness in the hydrogenation of styrene and the dechlorination of 4-chlorotoluene.^{69,146} Another innovative approach employs porous polytetrafluoroethylene (PTFE) as a support for a thin layer of Pd, ranging from 1 to 2 mm in thickness.¹⁴⁷ The inherent high porosity of PTFE enables a 12fold increase in the electrocatalytic surface area in comparison to conventional planar Pd membranes. This unique design minimizes the amount of Pd needed and also enhances the diffusion of reactants and hydrogen across the Pd layer, making it particularly advantageous for the hydrogenation of substrates like 1-hexyne. These cost-effective alternatives for hydrogenpermeable electrodes contribute positively to the scalability and economic viability of ePMR technologies.⁷⁰ Nevertheless, these new types of Pd-based hydrogen permeable membrane electrodes have not yet been fully explored, and it remains to see the potential of their large-scale applications.

Despite these promising advancements in Pd-based hydrogen permeable membrane electrodes with low amounts of Pd, their full potential, particularly in terms of large-scale applications, remains an area for future exploration. There exists a need to thoroughly investigate not only their catalytic efficiencies and durability under various operational conditions but also to assess the scalability of their manufacturing processes. This involves examining the cost-effectiveness of material synthesis, the stability of these membranes over extended periods, and their performance in diverse chemical environments. This comprehensive evaluation is essential to unlocking the full potential of these alternative Pd-based membrane electrodes for practical, large-scale hydrogenation applications.

5. CONCLUSION

In this Perspective, we present a side-by-side analysis of several representative examples of conventional electrocatalytic hydrogenation versus ePMR hydrogenation, underscoring the unique benefits conferred by the latter. ePMR distinguishes itself through the use of permeated hydrogen atoms for hydrogenation, which occurs in a separate chamber outside the electrochemical cell. This configuration substantially broadens the scope of the applicable solvents, electrolytes, and substrate concentrations. Moreover, it bypasses constraints related to solubilizing sufficient reactants in a protic electrolyte and simplifies both downstream product purification and electrolyte recovery. As the range of substrates amenable to ePMRbased hydrogenation continues to grow, future research should pivot toward tackling more intricate hydrogenation reactions. These include N2 reduction to ammonia, ester hydrodeoxygenation, asymmetric hydrogenation, and site-specific deuteration of molecules or drugs with pharmaceutical relevance. To improve hydrogenation efficiency and selectivity, a multipronged strategy is warranted, encompassing catalyst optimization, inclusion of more competent and versatile molecular catalysts, and meticulous control of electrochemical conditions (e.g., voltage and current). Further, the integration of Pd_m cathode hydrogenation with value-added anodic oxidation reactions and the implementation of dual hydrogenation offer substantial prospects for boosting the economic feasibility and overall energy efficiency. Additionally, utilizing advanced in situ spectroscopic techniques and computational tools to investigate the dynamic processes on Pd_m electrodes and determine the surface adsorbed intermediates will

contribute to a comprehensive understanding of the hydrogenation mechanisms. One pivotal concern that merits attention is the propensity for Pd_m electrodes to suffer hydrogen embrittlement due to continual hydrogen permeation. This could undermine the integrity of the hydrogen transport pathway and subsequently decrease the hydrogenation efficacy. To address this issue, there is a need for the development of Pd-based films or alternative hydrogen permeable membrane electrodes that resist embrittlement. Eventually, the potential for industrial adoption of ePMR hinges on its scalability and long-term operational stability.¹⁴⁸

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Notes

The authors declare no competing financial interest.

Biography

Yujie Sun received a B.S. degree in Chemistry from Fudan University in 2005 and a Ph.D. degree in Inorganic Chemistry with Prof. Claudia Turro at The Ohio State University in 2010. After conducting postdoctoral research in the group of Prof. Christopher J. Chang at the University of California, Berkeley and Lawrence Berkeley National Laboratory, he joined Utah State University as an Assistant Professor in 2013, moved to the University of Cincinnati as an Associate Professor in 2018, and was promoted to Professor in 2023. The research interests of the Sun group include the development and understanding of inexpensive materials and complexes for sustainable catalysis and biomedical applications.

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