Palladium (Pd) plays a significant role in substantial catalytic reactions. On account of the strong affinity for hydrogen, various Pd-based nanostructures with different shapes and sizes have been extensively utilized in hydrogenation reactions. In particular, Pd reveals extraordinary properties while interacting with hydrogen, including strong adsorption, barrier-less dissociation, and large storage of hydrogen under ambient temperatures and pressures.

Pd-based catalysts, such as Pd/C and Lindlar catalysts, have been widely used in the thermocatalytic hydrogenation industry, employing H2 as proton sources. During the hydrogenation process, H2 molecules split into proton adsorbates (H+) on the Pd active sites as shown in Figure 1A, which are typically in the form of metal nanoparticles, clusters, or single atoms immobilized on substrates, and then react with the surface-adsorbed reactants to form hydrogenation products. However, one of the main ways to obtain industrial H2 is natural gas reforming, which has brought about massive raw material consumption and emission of greenhouse gases. Therefore, seeking novel strategies for hydrogenation reactions based on green hydrogen sources is one of the vital developing tendencies in this field. Alternative (photo)electrocatalytic techniques have drawn increasing attention in hydrogenation reactions, as they can utilize renewable energy as the driving force and water molecules as the proton source. On a typical electrode using Pd-based materials as electrocatalysts, water molecules are first adsorbed on the Pd active sites, then reduced with electrons to form H+, as shown in Figure 1B. The H+ adsorbates will react with dissolved reactants at the interface to generate hydrogenated intermediates, followed by the release of reduction products. Pd-based electrochemical reduction systems have been widely investigated for the selective conversion of CO2, O2, aldehyde, and alkyne. However, one of the most severe problems is the hydrogen evolution side reaction, which severely decreases the faradic efficiency and energy efficiency. The solubility of reactants and the separation between hydrogenated products and electrolytes are other challenges to be resolved.

The Pd membrane electro-hydrogenation system is a novel technique designed to integrate the thermocatalytic and electrochemical hydrogenation routes. It is constituted of an electrochemical side and a hydrogenation side, separated by a Pd membrane, as shown in Figure 1C. The electrochemical side is in charge of reducing water molecules or protons from aqueous electrolytes (e.g., sulfuric acid or other alkaline solutions) to generate adsorbed H+ active species. As for the hydrogenation side, it is usually equipped with an organic solvent that conducts as the reactant medium. Active sites on the hydrogenation side are typically formed by surface modification of the Pd membrane or deposition of a second metal component. The pivotal function of the Pd membrane can be summarized in three aspects: (1) A conductive electrode to reduce water molecules to H+ on the electrochemical side. The as-formed H+ atoms are subsequently absorbed and stored in the palladium lattice. (2) A selective permeation membrane that allows H+ to diffuse from the electrochemical side to the hydrogenation side via a solution-diffusion mechanism. The selective permeation behavior originates from the unique octahedral holes in the face-centered cubic palladium lattice. (3) A firm support for stabilizing hydrogenation catalysts and transferring H+ to the active site to complete the selective hydrogenation of reactants. The Pd membrane electro-hydrogenation system separates the proton reduction and hydrogenation steps spatially, offering new opportunities in separately controlling the generation and utilization of H+ active species. For example, the efficiency of H+ production and transfer can be notably promoted by increasing the acidity of the electrolytes without affecting the structure of the hydrogenation side. It inherits the advantage of green hydrogen sources from the electrocatalytic reduction system but reduces the competition of the hydrogen evolution reaction. Meanwhile, the hydrogenation takes place in organic solvents rather than in electrolyte solution, which improves the solubility and mass transfer of reactants and provides ideal conditions for the direct preparation of high-purity organic products. Separating organic reactants from the electrolyte also allows higher ionic conductivity on the electrocatalytic side, contributing to reduced over-potential and improved energy efficiency.

Since the first Pd membrane electro-hydrogenation system was developed in 1996, great progress has been made, including the paired redox reactions between various Pd membrane hydrogenation reactions and oxidation reactions on the counter electrode, the application of deuterium reactions to synthesize pharmaceutical molecules, and the modification of secondary metals on the Pd membrane. Recently, Yuxuan Zhang and Nikolay Korrienko designed a novel Pd membrane electro-hydrogenation system that converted acetonitrile (CH3CN) into ammonia and acetaldehyde, achieving an ammonia production faradic efficiency of 60% at ~0.5 V versus Ag/AgCl reference electrode. The hydrogenation reaction took place via an imine hydrolysis pathway with a well-suppressed hydrogen evolution reaction in a CH3CN medium containing 0.2 vol % H2SO4 as shown in Figure 1D. In addition, to increase the density of surface electrocatalytic active sites, Pd nanospikes were electrodoped on the hydrogenation side of the Pd membrane. The protons from the acidic aqueous electrolyte can be reduced to active H+ atoms, which will gather at the surface of the Pd active sites exposed to the hydrogenation side and efficiently react with CH3CN. The nitrogen atom in the CH3CN molecule was firstly adsorbed on the Pd nanospikes to form CH2CN, and the oxygen atom was added to acetonitrile through nucleophilic attack by water as well as subsequent proton transfer. The intermediate then conducted several proton transfer processes to produce NH4+ (x = 1–3) and release acetaldehyde. Finally, the as-formed ammonia molecule was desorbed from the Pd membrane.

The onset potential of the system was improved for about 0.5 V compared with previous reports based on a three-electrode setup. Electrochemical and spectroscopic studies demonstrated that the improvement in onset potential and the avoidance of hydrogen evolution side reaction could be contributed to the thermodynamic potential determined by the Pd hydrogenation process. The authors constructed an in situ infrared spectroelectrochemical cell and successfully probed a series of reaction intermediates by infrared spectroscopy in an attenuated total reflection configuration, including the CH3CN# and the first hydrogenated *NH4 species, on the surface of the Pd membrane. The results provided a molecular schematic behind the observed reactivity in the Pd membrane electro-hydrogenation system. And the reaction could proceed at room temperature, which is much lower than the previous requirement of at least 373 K. The maximum ammonia partial current density was about 5 mA cm–2, a moderate value among all electrochemical ammonia production reports, indicating that the ammonia production rate still needs substantial improvements to achieve application requirements. Nonetheless, the work established a novel hydrogenation route for nitrite and extended the scope of the Pd membrane electro-hydrogenation system from unsaturated carbon compounds to nitrogen-containing compounds.

There still remain some challenges to be resolved for the Pd membrane electro-hydrogenation system.

Firstly, the abundance and reactivity of the reaction active sites exposed to electrochemical and hydrogenation sides are important in the Pd membrane electro-hydrogenation systems, which primarily depend on the structural engineering of the Pd membrane. The size, morphology, exposed crystal lattice of the Pd membrane, and constitution of the surface-immobilized catalysts substantially influence the selectivity and efficiency of the electro-hydrogenation reactions. Currently, the structure and composition of the Pd membrane on the hydrogenation side are hard to be regulated, while a smooth Pd surface is often applied to the electrochemical side. The intrinsic hydrogen storage property of the Pd membrane can also lead to brittleness, which will destroy the hydrogen transfer path and substantially cut down the hydrogenation performance.
concerns above, constructing Pd-based multi-metal nanostructures, such as the Pd-based alloy (Pd-Ag and Pd-Au), introducing special Pd-organic interfacial interactions, and regulating the pH and the applied current of the electrochemical side are promising strategies to regulate the electronic structure, coordination environment and enhance the mechanical strength of the Pd membrane.4,5 Restraining the potential hydrogen evolution reaction in the system is another challenge that can be potentially solved by the strategies above and the design of electrolytes on the electrochemical side.

Besides, the total faradic efficiency of most reported Pd membrane electro-hydrogenation systems can hardly reach 100%, possibly due to the slow migration and irreversible storage of H* in the palladium lattice. The intrinsic H* transfer properties and the underlying relationship between H* generation, storage, and reaction through the palladium lattice should be studied thoroughly via advanced spectroscopic and chromatographic technologies. Optimizing the H*-directed migration will be a breakthrough in enhancing the limiting current density to a more practical level.

The type and added value of the products from the hydrogenation side require improvement. Organic molecules relevant to producing biofuels and pharmaceutical medicine can be introduced to the Pd membrane electro-hydrogenation systems. For instance, incorporating deuterium atoms into the electrochemical side might be helpful for the selective synthesis of valuable deuterated drug molecules. Other challenging nitrogen-related reactions (e.g., nitrogen fixation) can also be considered for implementation in the systems. The selection of reaction medium on the chemical side is also critical in realizing different types of hydrogenation processes. Organics, protonic solutions, and other reaction mediums should be amply studied to better coordinate different reactants and reactions.

In addition, coupling the Pd membrane electro-hydrogenation system with value-added oxidization reactions (such as glycerol and benzyl alcohol selective oxidation) instead of water oxidation is supposed to improve the full cell economy and energy efficiency.

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DECLARATION OF INTERESTS
The authors declare no competing interests.