EDITORIAL

Hydrogen generation from formic acid: A CO_2-to-power loop route towards hydrogen economy

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The hydrogen economy is recently an ongoing topic of interest, which refers to a vision of utilizing hydrogen as a widespread carbon-free energy carrier. As a key technology for reaching net-zero CO_2 emissions, hydrogen can be widely used as the fuels for heating and transportation, chemicals feedstock for industrial productions, and medium for energy storage. At present, water electrolysis driven by the green electricity is broadly accepted as a feasible approach for hydrogen generation, and the hydrogen-oxygen fuel cells are developing as the efficient terminal energy-conversion system. However, the construction of hydrogen network suffers from a wide gap between the gaseous hydrogen generation and consumption, involving the intrinsic problems of low mass density, poor safety, and high cost during the hydrogen storage and transportation.

Despite extensive efforts devoted to the high-pressure tanks for compressed hydrogen storage, the practical aspects in terms of high cost and technologies are rarely addressed. Liquefied hydrogen storage with a higher density is also considered, which is however cost prohibitive by using the cryogenic vessels to minimize evaporation at -252.8°C. Besides, the common phenomenon of hydrogen embrittlement also threatens the whole hydrogen processes of production, transportation, and storage. It is well known that the hydrogen explosion limit is wide as 4.0 ~ 75.6 vol.%. Thus, minor leakage of hydrogen in enclosed spaces potentially give rise to severe life, infrastructure or environmental damages. Therefore, hydrogen storage in a compact, cost-effective, and safe manner is of primary concern to make the hydrogen economy possible.

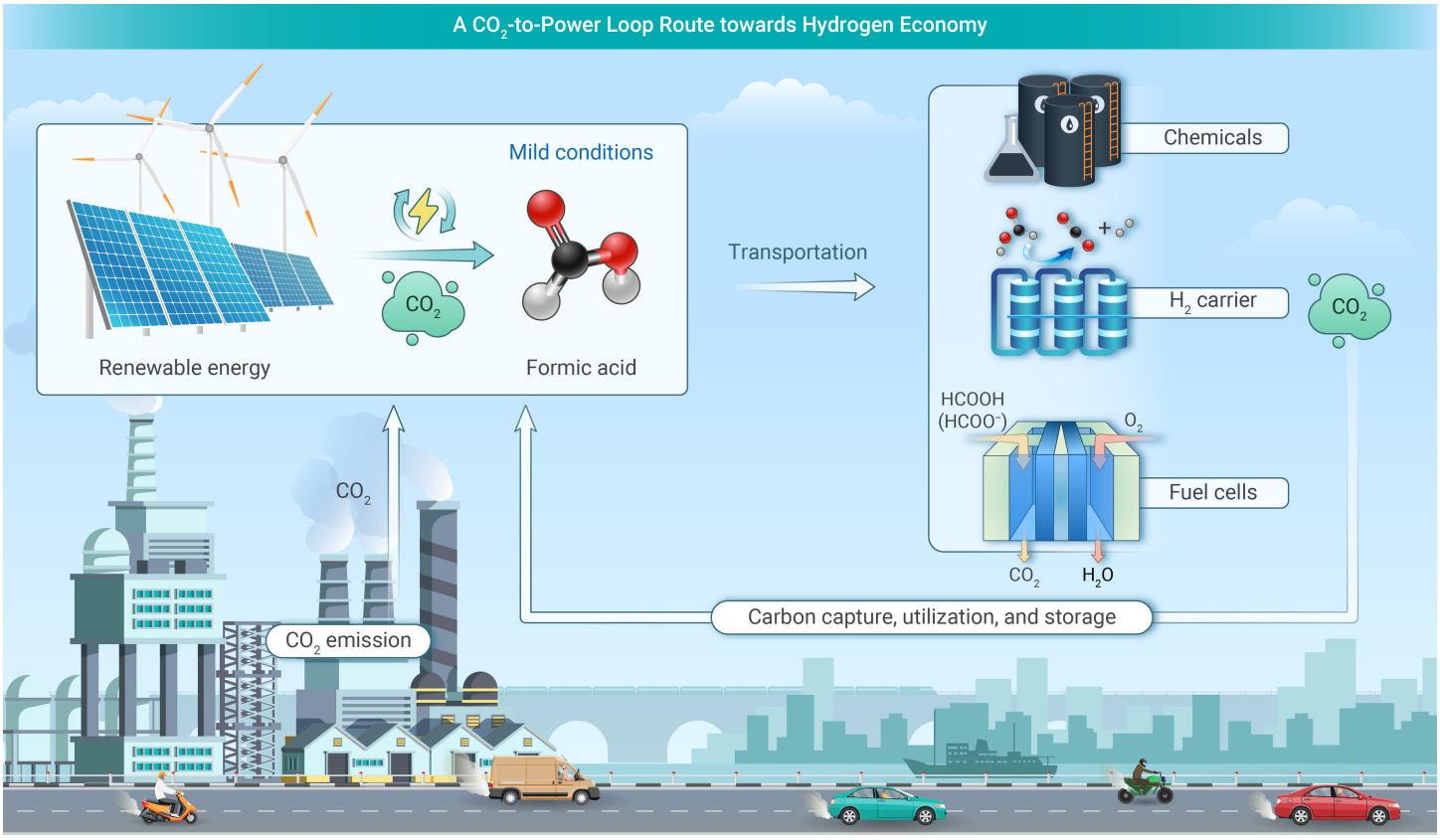

Figure 1. The schematics of a CO_2-to-power loop system.

To date, several alternative strategies have been proposed to address the intrinsic issues for gaseous hydrogen. The solid-state hydrogen storage technique is one of attractive approaches by physically or chemically compacting hydrogen in solid material, showing higher safety and volumetric capacities relative to the compressed gaseous storage. In case of physical storage, the materials mainly feature high surface areas with sufficient adsorption sites, such as zeolites, porous carbon materials, and metal organic framework (MOF).[1] These processes possess rapid kinetics during the reversible adsorption and desorption with negligible hydrogen loss. Recently, emerging research interests are also focused on chemical adsorption using the metal hydrides. For example, magnesium-based hydride, a potential candidate with the merits of low cost and abundant resource, can achieve a high hydrogen storage capacity of 7.7 wt.%.[2] However, the critical issues remain regarding the easily oxidized surface and harsh conditions required for reversible adsorption/desorption of maximum capacity.

Thoughts have emerged that an ideal energy carrier is preferably high-density liquid phase as the petroleum, which can be operatively transported and stored by pipelines. To this end, liquid organic hydrogen carriers have been considered as an attractive option. They can be transported and stored with a higher capacity of hydrogen at normal pressure, which can also ease

the issue of severe hydrogen embrittlement in the form of organic molecules. Currently, a variety of liquid organic hydrogen carriers have been investigated, including methanol, formic acid (FA), borane, hydrazine hydrate, and so forth. On-site generation of hydrogen can be realized via catalytic reactions, contributing to the ready use and substantial alleviation of hydrogen storage risks. In addition, no charging process is required compared to the solid-state storage, showing technical flexibility and simplification.

Among the various organic hydrogen carriers, FA has attracted extensive research devotion due to the non-toxicity and unique capacity of hydrogen uptake/release at normal pressure and relatively low temperature (e.g., 25-80°C). The fast dehydrogenation of FA under mild conditions provides the distinct advantages of cost-effectiveness and practical flexibility compared to other liquid hydrogen carriers. Catalysts including the homogeneous and heterogeneous phases play a crucial role in the rapid FA dehydrogenation. The organometallic homogeneous catalysts generally show fast dehydrogenation rate due to the high utilization of active sites. For instance, the iridium-based homogeneous catalyst exhibit a high turnover frequency (TOF) values of 13290 h^{-1} at 353 K.[3] Nevertheless, it is challenging to be scaled up due to the difficulty of separation and environmental pollutions. As a comparison, these issues can be well overcome by the heterogeneous catalysts, which are mainly based on efficient noble metals (e.g., Au, Pd, Pt, or alloys). For example, the Pd-CeO_X nanoparticle supported by zeolite nanosheets showed a TOF of 5974 h^{-1} at 323 K.[4] Nevertheless, the catalytic activity and long-term stability of heterogeneous catalysts are in general inferior to homogeneous catalysts due to the CO or other intermediate poisoning. Therefore, the development of low-cost heterogeneous catalysts is still desirable yet challenging for fast and stable FA dehydrogenation.

Importantly, electrochemical CO_2 reduction reaction (CO_2RR) provides a promising method for producing FA or formate at low overpotentials. Compared to traditional energy-intensive routes, the co-electrolysis of CO_2 and H_2O to yield FA can be coupled with the carbon capture, utilization, and storage (CCUS) systems to further alleviate the excessive CO_2 emissions. For example, high-purity FA (~100% wt.%) can be produced *via* CO_2RR by using an all-solid-state electrochemical system, which is highly efficient by eliminating the energy-intensive distillation process.[5] The decarbonized FA can be safely transported to the terminal systems and used as the basic chemicals, the precursor of hydrogen, or fuels for direct FA or formate fuel cells (FAFCs/DFFCs) to provide power. It should be noted that the power density of FAFCs/DFFCs is still lower than that of hydrogen-oxygen fuel cells due to the sluggish reaction kinetics of formate or FA oxidation. However, taking the overall cost of gaseous hydrogen into consideration, the FAFCs/DFFCs could possess the economic benefits. Finally, the released CO_2 can be recycled *via* CCUS, building a sustainable CO_2-to-power loop system by forming a carbon-neutral cycle (Figure 1). In particular, the integrated CO_2 capture and electrochemical conversion has attracted research interest from the perspective of feasible and sustainable benefits, considering the energy-intensive capture processes. According to the vision planning, the technologies including CCUS, CO_2-to-FA conversion, FA dehydrogenation, and FAFCs/DFFCs are the key steps to put this net- zero target by 2060 within reach.

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AUTHOR CONTRIBUTIONS

Zhenyi Yang: Conceptualization, Investigation, Formal analysis, Writing-original draft, and Visualization. **Yibin Chen:** Investigation, Formal analysis, Writing-original draft. **Yu Zhang:** Conceptualization, Formal analysis, Resources, Supervision, Funding acquisition, Writing–review & editing.

DECLARATION OF INTERESTS

The authors declare no competing interests.