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Perspective

Electrochemical conversion of carbon dioxide in molten salts: *In-situ* and beyond

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The state-of-the-art industry based on carbon-intensive energy causes major concerns on energy and environmental sustainability. Carbon neutrality is now a worldwide consensus and an imperative task. Efficient capture and/or conversion of carbon dioxide (CO_2) is key-enabling to achieve carbon neutrality. Challenges of the aforenamed task lie in the chemical inertness of CO_2 and costly separation of CO_2 from flue gases. Capture and conversion of CO_2 on the occasions of generation, namely *in-situ* CO_2 conversion, are highly desired.

Carbon cycle in the ecosystem is governed by a reversible transformation between aqueous carbonates and bicarbonates at ambient conditions. Taking sodium carbonate/bicarbonate as the model, the change of Gibbs free energy on the carbonate-to-bicarbonate transformation is $-26\ \mathrm{kJ\ mol^{-1}}$ at 25 °C. The reaction remains in a dynamic equilibrium to maintain a stead state of carbon in the ecosystem. The chemistry of carbonates regarding absorption of CO_2 becomes highly thermodynamically spontaneous and highly exothermic at elevated temperatures, as shown in the inset of Fig. 1(a).

Molten salt electrochemistry has been commercialized to extract Al metals, in which alumina feedstock dissolves in molten fluoride with the assistance of cryolite. Alumina and CO_2 can be regarded as "analogues" in molten salts. Molten salts have good solubility of O^{2-} and large electrochemical windows to accommodate electro-deoxidation, hence making molten salt electrochemistry a suitable platform for *in-situ* CO_2 conversion. The capture of CO_2 by molten salts containing O^2 is highly exothermic, compensating heat loss of high-temperature molten salts and ensuring a high energy efficiency. Molten salts with large electrochemical windows, high solubility of O^{2-} and CO_3^{2-} are essential for *in-situ* CO_2 conversion. In this regard, molten carbonates and molten chlorides are suitable media for *in-situ* CO_2 conversion. For example, the solubility of $CaCO_3$ in molten $CaCl_2$ is as higher as 32 mol% at 650 °C, based on the phase diagram of $CaCl_2$-$CaCO_3$.

Most of metals tend to oxidize and dissolve in molten salts upon the oxygen evolution reaction (OER) [1]. Carbon-based anodes are hence used as anode in molten salt electrolysis of metal oxides for metal extraction, causing huge emissions of CO_2 at the carbon anodes [2,3]. Elaboration of O^{2-} in molten salts is essential to facilitate the electrolysis of metal oxide for metallurgy and also to alleviate emissions of CO_2 at carbon anode. A recent report shows that the above two processes are connected in serial in molten salts for advanced metallurgy and *in-situ* CO_2 fixation [4]. Upon electrolysis of GeO_2 in molten NaCl-$CaCl_2$ at 750 °C for Ge extraction, cathodic Ge and anodic CO_2 at a graphite anode are generated. By simply adding extra O^{2-} into molten salts, the anodic CO_2 is captured by O^{2-} in the melts and transformed into CO_3^{2-}. The generated CO_3^{2-} and GeO_2 are then electrochemically reduced to cathodic Ge nanoparticles encapsulated in carbon nanotubes and anodic O_2. These results highlight that molten salt electrochemistry is capable of *in-situ* CO_2 conversion.

Methane (CH_4) is a high-quality hydrogen source, and methane steam reforming ($CH_4 + 2H_2O = CO_2 + 4H_2$) is the main industrial hydrogen production. High-temperature electrochemistry activates C–H by raising temperature and reduces apparent activation energy by overpotentials, which is a new way of CH_4 activation and transformation [5,6]. Anodic oxidation of CH_4 coupling with cathodic reduction of CO_2 or H_2O shows promise in efficient utilization of carbon-based fuels. However, CH_4 is easy to be over-oxidized to CO_2 and easy to crack to carbon, resulting in inconvenient CO_2 emissions and low conversion efficiency.

In-situ electrochemical conversion of CO_2 in molten salts promises a carbon-emissions-free CH_4 conversion to produce hydrogen [7]. As can be seen in Fig. 1, splitting of CH_4 is spatially deconvolved into anodic oxidation of CH_4 and *in-situ* CO_2 conversion, which is mediated by prompt absorption of anodic CO_2 by molten salts with the assistance of present O^{2-} in the melts (as highlighted in red in Fig. 1a). The core innovative idea is that H is completely dissociated from CH_4 to generate H_2 in high temperature molten salt system, while C from CH_4 is completely oxidized to CO_2 and absorbed in molten salt electrolyte to transfer to cathode, and finally reduced and fixed to carbon. By introducing alkaline earth metal oxides into molten salt electrolyte to absorb anodic CO_2, electrochemical splitting of CH_4 at 500 °C is realized. The overall reaction is CH_4 cracking, which is the most energy-saving pathway for CH_4 conversion (Fig. 1b). Hydrogen production and carbon deposition occur at the anode and cathode, respectively. The spatial isolation of hydrogen from carbon deposition ensures a stable hydrogen evolution. Anodic oxidation of CH_4 occurs in potential much negative than OER, making most of com-

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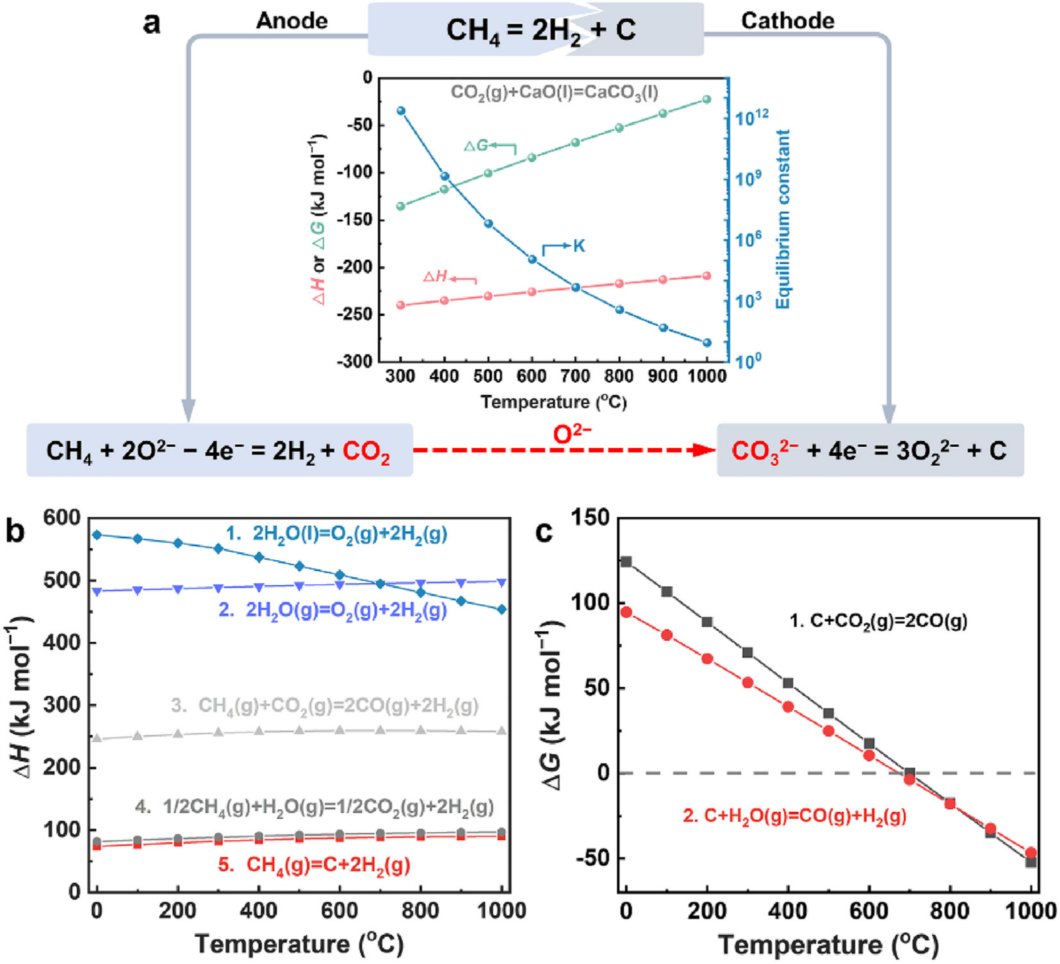

Fig. 1. (a) *In-situ* electrochemical conversion of CO_2 in molten salts for carbon-emissions-free CH_4 conversion. The inset shows the thermodynamic on absorption of CO_2 by O^{2-}-containing molten salts; (b) total energy consumption on some typical hydrogen-production methods; (c) introduction of steam or carbon dioxide to eliminate cathodic carbon deposition.

mon metals being stable anode for anodic CH_4 oxidation. Introduction of steam or carbon dioxide to eliminate cathodic carbon deposition for continuous operation is thermodynamically possible at temperatures higher than 700 °C (Fig. 1c). Sophisticated engineering of reaction interface for CH_4 oxidation and CO_2 reduction is essential to produce CO, syngas and ethene, which deserves further investigation in future. The protocol can also be extended to convert other alkanes (e.g., ethane).

By mimicking molten salt electrolysis of alumina for Al extraction and exploiting good absorption of CO_2 by molten salts, *in-situ* electrochemical CO_2 conversion in molten salts is realized [4]. This protocol is then used to eliminate accompanying CO_2 emissions upon CH_4 conversion. By coupling *in-situ* CO_2 conversion with CH_4 oxidation in molten salts, a CO_2-free generation of hydrogen from methane is achieved. In higher temperatures, generation of CO from reduction of CO_2 and oxidation of CH_4 is thermodynamically more favorable. Therefore, typical carbon-based energy small molecules, i.e., $CO/CO_2/CH_4$ can be processed and manipulated in molten salt electrolyzer. Molten salts bridge the temperature gap between low temperature electrolytes (aqueous solutions and ionic liquids) and high temperatures (solid oxide electrochemical cells), and might provide new opportunities on efficient utilization of carbon-based fuels. C–C coupling and operando observations on surface/interface in molten salt electrolyzer are yet to be implemented [8], which is the central focus of future research. Electrochemical conversion of CO_2 in molten salts successfully extends the scope of molten salt electrochemistry from metallurgy to conversions of carbon dioxide and methane, endowing molten salt electrochemistry with a new scientific meaning of generic technology towards carbon neutrality.

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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