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ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE

Background :

The rapid and excessive usage of fossil fuels, such as coal, oil, and natural gas, has been the reason of modern industrialization and energy production. However, this reliance on fossil fuels has come at a significant environmental cost. When combusted, these fuels release carbon dioxide (CO_2) into the atmosphere. The accumulation of CO_2 is a main reason of climate change, leading to global warming and its associated adverse effects.

The increase in the atmospheric concentration of CO_2 is largely attributed to anthropogenic factors. Activities like the burning of fossil fuels for electricity, transportation, and industry have substantially contributed to elevated CO_2 levels. Deforestation further adds to the issue by reducing the Earth's capacity to absorb CO_2.

Controlling CO_2 emissions is imperative to reduce climate change and its dangerous consequences. By transitioning to cleaner and more sustainable energy sources, improving energy efficiency, and implementing carbon capture and storage technologies, we can reduce the release of CO_2 into the atmosphere. These measures are critical for safeguarding the environment and ensuring a habitable planet for future generations.

The electrochemical reduction of carbon dioxide (CO_2) is a promising approach for tackling climate change and producing valuable fuels and chemicals. This process involves using electrical energy to drive the conversion of CO_2 into products like carbon monoxide (CO) or hydrogen (H_2). Solid oxide electrolysis cells (SOECs) and other electrochemical systems are the leaders of this technology, offering high efficiency and versatility in product generation. These systems not only reduce greenhouse gas emissions but also provide a means of energy storage and the production of clean fuels.

The researchers explored the Hybrid Electro-thermochemical Looping process to tackle the Boudouard reaction in carbon dioxide catalytic reactions. This reaction typically leads to carbon deposits that can harm electrode efficiency, especially in nickel electrodes.

However, in this hybrid process, the Boudouard reaction is intentionally used to recover carbon deposits, resulting in amorphous carbon, graphite, and carbon nanotubes.

From a thermodynamic standpoint, the Boudouard reaction is more likely to occur than other electrolytic methods for carbon dioxide conversion. Unlike directly converting carbon dioxide into solid carbon, this process converts it into carbon monoxide under relatively moderate conditions. The research shows that solid carbon production becomes dominant only at temperatures above 971 K, while higher temperatures exceeding 700 °C favor carbon monoxide formation. Therefore, the overall system can operate at lower temperatures than a Solid Oxide Electrolysis Cell (SOEC).

Processes :

1. **Metallothermic reactions :**

   Metallothermic reduction is a process where a metal is used as a reducing agent to obtain a specific metal or compound from source materials like oxides or halides. In simple terms, it's a method for producing a desired metal or compound by using another metal to reduce the source material. It follows a simple equation similar to displacement reactions as:

   $MX + R \rightarrow RX + M$

   Where MX is feed material, R is reducing agent, RX is the by-product, M is the desired metal/element obtained.

   LIMITATIONS :

   - **Complex Operational Techniques.**
   - **Use of Expensive Reductants like Lithium, Sodium, Magnesium & Calcium.**
   - **Reducing agents such as Ferrocene cause Environmental pollution.**

   To overcome these limitations, we use electrochemical approaches.

2. **Reduction via Solid Oxide Electrolytic Cells (SOECs) :**

   Many studies have explored the use of Solid Oxide Electrolysis Cells (SOECs) for different purposes, like steam electrolysis, carbon dioxide electrolysis, and co-electrolysis of both gases to create hydrogen, carbon monoxide, or syngas. In carbon dioxide electrolysis with SOECs, the cathode facilitates the reduction of carbon dioxide, leading to the production of carbon monoxide and solid carbon.

GENERATION OF CARBON NANOTUBES (CNTs):
In this study, researchers successfully created multiwalled carbon nanotubes within a range of 2 μm from electrodes by co-electrolyzing carbon dioxide and steam while applying a strong cathodic polarization. They used a standard setup with a yttria-stabilized zirconia (YSZ) electrolyte, a Ni−YSZ cathode, and a lanthanum strontium manganite (LSM)−YSZ anode. The electrolytic cell worked at a high temperature of 875°C and a current density of 2.25 A cm^{-2}, using a gas mixture containing 45% H_2O, 45% CO_2, and 10% H_2. The gas mixture was introduced into the cathode side at a flow rate of 25 L h^{-1}, and calculations showed a gas conversion rate of 67%.

Transmission electron microscopy (TEM) images were used to confirm that the carbon nanotubes created had a hollow structure with a diameter of about 20 nanometers. These nanotubes also contained nanoparticles at their ends, and further analysis identified the composition of these nanoparticles as Zirconia through Energy-Dispersive X-Ray analysis.

Mechanism :

- In Solid Oxide Electrolysis Cells (SOECs), under low oxygen levels on the electrode surface, zirconia nanoparticles act as catalysts to convert carbon monoxide produced during SOEC operation into carbon nanotubes. This happens when the oxygen partial pressure at the interface between the Ni−YSZ cathode and YSZ electrolyte drops to a sufficiently low level.

- As oxygen partial pressure decreases, the presence of oxygen defects near the electrolyte− electrode interface increases. This is achieved by increasing the cathode overpotential.

- At 850°C and 2.25 A cm^{-2}, the oxygen partial pressure at the YSZ interface is extremely low, approximately 10−27 atm. Strong cathodic polarization at the interface partially reduces zirconia, giving it electronic conductivity.

- Normally, zirconia has only ionic conductivity. However, the partially reduced zirconia nanoparticles become catalysts with both ionic and electronic conductivity, promoting the growth of carbon nanotubes.

- Under low oxygen levels on the electrode surface, carbon monoxide is adsorbed on zirconia and catalytically decomposed. Meanwhile, oxygen ions fill oxygen vacancies in zirconia, and carbon atoms deposit onto zirconia's surface.

- This continuous process leads to the formation of carbon nanotubes. As carbon nucleation progresses, the newly formed carbon deposits integrate into the root of the nanotubes, raising the zirconia nanoparticles.

There are several challenges associated with Solid Oxide Electrolysis Cells (SOECs):

a) **High Operating Temperatures:** SOECs require extremely high operating temperatures, which causes materials to deteriorate over time. Hence maintenance needs increase and affects durability and economic feasibilty.

b) **Catalyst Development:** The production and deposition of carbon materials often lead to their adherence and buildup on the catalyst material's surface thereby diminishing the number of active sites accessible for catalytic reactions.

c) **Cost:** The initial cost of SOECs is high. Research wishes to lower production costs by using innovative manufacturing techniques and advanced materials engineering.

3. CO_2 Reduction using Hybrid Electro-thermochemical Looping :

It follows a two-step mechanism with the first step as reduction of CO_2 into CO and Oxygen at high temperature SOEC. The second step is the Boudouard reaction where Carbon Monoxide goes disproportionation reaction at higher temperatures.

In the research on Hybrid Electro-thermochemical Looping, scientists usually try to avoid the Boudouard reaction when working with carbon dioxide in catalytic reactions. This is because the Boudouard reaction leads to the formation of carbon deposits, which can harm the active sites and porous structure of the electrode. Nickel electrodes are highly effective in breaking down carbon-containing gases, but carbon deposits can make the nickel particles detach from the electrode, causing damage.

Step 1 : $CO_2(g) \rightarrow CO(g) + \frac{1}{2} O_2(g)$

Step 2 : $CO(g) \rightarrow C(s) + \frac{1}{2} O_2(g)$ (disproportionation reaction)

However, in the hybrid electro-thermochemical looping method, the Boudouard reaction is used deliberately to help recover the carbon deposits produced during carbon dioxide reduction. These carbon deposits can include amorphous carbon, graphite, and carbon nanotubes. From a thermodynamic perspective, the Boudouard reaction is more likely to occur than other methods for converting carbon dioxide. Unlike directly converting carbon dioxide to solid carbon, turning it into carbon monoxide can be done under milder conditions.

By comparing the Gibbs free energy, it's clear that the production of solid carbon only becomes the main reaction when the temperature goes above 971 K in the electrolytic system. However, with the Boudouard reaction, at higher temperatures exceeding 700 °C, the positive entropy contribution becomes dominant, causing the reaction to naturally shift towards forming carbon monoxide. This means that very high temperatures are not ideal for producing solid carbon. Consequently, the system can operate at a lower temperature compared to Solid Oxide Electrolysis Cells (SOEC).

CONCLUSION :

Practical applications include formation of solid carbon materials with high added values like graphite, graphene, CNTs, CNFs etc. Graphite plays a crucial role in storing and releasing electrical energy in batteries. With the increasing shift towards electric vehicles (EVs) and hybrid electric vehicles (HEVs), the demand for graphite is expected to grow significantly. Global demand for graphite is projected to reach 1.9 million tons by 2028, and the battery-grade graphite market is set to be worth around $14 billion by 2025.

Although natural graphite is less expensive, the price for natural flake graphite used in batteries is approximately $1500 per metric ton. However, when this graphite is further processed into coated spherical purified graphite (CSPG) for high-power lithium battery electrodes, the profit margins increase substantially, with CSPG potentially reaching a selling price of up to $20,000 per metric ton.

The current graphite production industry has complex production processes and significant environmental impacts due to emissions and energy intensity. Electrolyzing carbon dioxide to synthesize graphite offers a more sustainable approach, utilizing industrial exhaust gases as feedstock and alternative and renewable energy sources for thermal and electrical energy.

In summary, extensive research has been conducted on various methods to turn carbon dioxide into solid carbon using electrochemical processes. These methods include solid oxide electrolysis cells (SOEC) and the hybrid electro-thermochemical looping approach. While significant progress has been made in understanding the product formation mechanisms, further investigation is needed to push the field forward. This could involve exploring different catalyst materials, refining reaction conditions, and enhancing the efficiency and selectivity of carbon dioxide reduction. Ongoing research in this area holds the potential to advance the development of electrochemical techniques for converting carbon dioxide into solid carbon, contributing to environmental and energy solutions.

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