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Electrochemical Conversion of CO_2 using Silver Nanoparticles: Voltage Regulation Effects

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ABSTRACT

Electrochemical conversion of CO_2 into value-added products presents a promising route for carbon recycling and climate mitigation. Silver nanoparticles (AgNPs) have emerged as highly selective and efficient catalysts for the reduction of CO_2 to carbon monoxide (CO) due to their favorable surface properties and catalytic activity. This study investigates the role of voltage regulation in optimizing the performance of AgNP-based electrochemical cells for CO_2 reduction. Key parameters such as applied voltage, current density, and electrolyte composition were systematically varied to assess their impact on Faradaic efficiency, product selectivity, and catalyst stability. The results demonstrate that precise voltage control significantly enhances CO production while minimizing hydrogen evolution, a common competing reaction. At optimized conditions, AgNPs achieved CO Faradaic efficiencies exceeding 70% under pressurized CO_2 environments, with stable performance over extended operation periods.The findings underscore the importance of voltage regulation in tuning the electrochemical microenvironment, thereby improving the accessibility of CO_2 at the catalyst surface and suppressing side reactions. This work contributes to the development of scalable and energy-efficient electrochemical systems for sustainable CO_2 utilization.

Keyword: Electrochemical CO_2 reduction, Silver nanoparticles (AgNPs), Voltage regulation, Electrocatalysis, Faradaic efficiency

I. Introduction

The electrochemical reduction of carbon dioxide (CO_2) offers a compelling pathway to mitigate climate change by converting a greenhouse gas into valuable chemicals and fuels[1-4]. Among the various electrocatalysts explored, **silver nanoparticles (AgNPs)** have emerged as a standout candidate due to their high selectivity for converting CO_2 into carbon monoxide (CO) under mild conditions[5-7]. Recent studies have demonstrated that **voltage regulation plays a pivotal role** in steering the reaction kinetics and product distribution during CO_2 electro reduction. By fine-tuning the applied potential, researchers can influence the formation of key intermediates such as *COOH and *CO, suppress competing reactions like hydrogen evolution, and optimize Faradaic efficiency[8-10]. Silver's unique surface properties-

especially when engineered at the nanoscale-enable enhanced mass transport and active site exposure, which are critical for achieving high conversion rates[11-12]. For instance: At voltages around **-1.6 V vs. RHE**, CO production peaks due to favorable intermediate coverage. Lower overpotentials reduce hydrogen evolution, improving CO selectivity. Particle size and dispersion of AgNPs further modulate activity and efficiency[13-14]. This voltage-dependent behavior not only deepens our understanding of electrocatalytic mechanisms but also opens doors to scalable, sustainable CO_2 utilization technologies. As the world seeks carbon-neutral solutions, silver nanoparticle - based systems-optimized through voltage control-could become a cornerstone of future green chemistry[15].

II. Methodology

II A. Experimental Setup

Electro catalyst Preparation:

- Silver nanoparticles (AgNPs) are synthesized, often ligand-free, and supported on conductive substrates like carbon.
- Particle size control (typically 10–30 nm) is crucial for optimizing activity and selectivity.

Electrochemical Cell Configuration:

A three-electrode system is used:

- **Working electrode**: AgNP-coated substrate
- **Counter electrode**: Platinum or graphite
- **Reference electrode**: Ag/AgCl or reversible hydrogen electrode (RHE)
- Electrolyte: Typically 0.1 M $KHCO_3$ saturated with CO_2

Voltage Regulation and Measurement Techniques

- **Applied Potential Range**:
  - Voltage is varied from 0 V to −1.99 V vs. RHE to study its effect on product selectivity and reaction kinetics.
  - CO production peaks around −1.6 V vs. RHE, while hydrogen evolution dominates at more negative potentials.

- **Techniques Used**:
  - **Linear Sweep Voltammetry (LSV)**: To identify onset potentials and current response
  - **Chronoamperometry**: For steady-state current measurements over time
  - **Gas Chromatography (GC)**: To quantify CO and H_2 production

Reaction Mechanism Insights

- **Key Intermediates**:
  - $*CO_2^-$, *COOH, and *CO are involved in the multistep reduction pathway.
  - Formation of *COOH is voltage-dependent and becomes favorable near −1.1 V vs. RHE3.

- **Selectivity Trends**:
  - At moderate voltages (-1.0 to -1.6 V), silver shows high selectivity for CO (>90% Faradaic efficiency).

- At higher over potentials, H_2 evolution increases due to saturation of *H species on the surface.

Voltage-Dependent Kinetics

- **Activation Energy Calculations**:
  - Computational studies show that voltage influences the activation barriers for COOH* and HCOO* formation.
  - COOH* becomes kinetically favored over H_2 and formate at specific voltages, explaining silver's CO selectivity.

- **Surface Coverage Effects**:
  - Surface coverage of intermediates like $*CO_2^-$ and *CO increases with voltage up to a threshold, then declines due to competing reactions.

II B. Why Silver Nanoparticles Are Effective

- **High Selectivity for CO Production**:
  - Silver is one of the most selective metals for converting CO_2 to carbon monoxide (CO), a valuable feedstock for syngas and chemical synthesis.
  - AgNPs outperform bulk silver in CO selectivity, especially at moderate over potentials.

- **Size -Dependent Activity**:
  - 5 nm AgNPs show up to **10× higher CO_2 conversion rates per unit surface area** compared to bulk silver.
  - This enhancement is attributed to optimal binding energies of reaction intermediates, which follow a "volcano plot" trend with particle size.

- **Surface Area and Dispersion**:
  - Nanoparticles offer a high surface-to-volume ratio, increasing the number of active sites.
  - Ligand-free, carbon-supported AgNPs maintain high dispersion and stability, even at low silver loadings.

Mechanistic Role in CO_2 Reduction

- **Intermediate Stabilization**:
  - AgNPs stabilize key intermediates like $*CO_2^-$ and *COOH, facilitating their transformation into *CO.
  - The optimal particle size tunes the binding energy of these intermediates, enhancing reaction kinetics.

- **Voltage-Responsive Behavior**:
  - At voltages around −1.6 V vs. RHE, AgNPs reach peak CO production efficiency.
  - At higher voltages, hydrogen evolution competes, reducing CO selectivity.

Additional Insights

- **Syngas Tuning**:
  - AgNPs can produce a tunable H_2:CO ratio (e.g., 2.9:1), useful for downstream syngas applications.

- **Catalyst Design**:
  - AgNPs are often integrated into composite systems (e.g., Cu/CuO–Ag) to promote C–C coupling and generate C_2+ products like ethylene and ethanol.

II C. Mechanism of CO_2 electrochemical reduction using silver nanoparticles (AgNPs):

Step-by-Step Reaction Mechanism

The reduction of CO_2 to CO on silver involves a **multi-step pathway** with key intermediates:

1. **CO_2 Adsorption**:
   - CO_2 molecules dissolve in the electrolyte and adsorb onto the AgNP surface.
   - The first electron transfer forms a surface-bound radical anion:

2. **Formation of Carboxyl Intermediate**:
   - The adsorbed CO_2^- reacts with a proton (from water or electrolyte) to form *COOH:

3. **CO Formation**:
   - A second electron transfer reduces *COOH to *CO.

4. **CO Desorption**:
   - The *CO intermediate desorbs from the surface:

Voltage Effects on Mechanism

- **Optimal Voltage Range**:
  - CO production peaks around **−1.6 V vs. RHE**. At this potential:
    - Surface coverage of *CO_2^- and *CO increases
    - Faradaic efficiency for CO is highest

- **Competing Reaction**: Hydrogen Evolution Reaction (HER)
  - At more negative voltages, HER becomes dominant:

- **Surface Coverage Dynamics**:
  - *COOH coverage peaks at **−1.06 V vs. RHE**
  - *H coverage increases at high overpotentials, reducing CO selectivity

Why Silver Nanoparticles Excel

- **Intermediate Stabilization**:
  - AgNPs stabilize *COOH and *CO without over-binding, allowing efficient desorption.

- **Size -Tuned Reactivity**:
  - Smaller AgNPs (10–30 nm) offer optimal binding energies and higher activity than bulk silver

- **Local Environment Effects**:
  - Surface charge, pH, and mass transport near AgNPs influence reaction kinetics and selectivity

II D. Fundamental Equation: Standard Cell Voltage

The **standard cell voltage** $E_{cell}^0=E_{cathode}^0-E_{anode}^0$ is calculated using the standard reduction potentials of the cathode and anode:

$E_{cell}^\circ=E_{cathode}^\circ-Eanode^\circ$

$E_{cathode}^\circ$: Standard reduction potential of the cathode

- E_{anode}° : Standard reduction potential of the anode
- Measured in volts (V)
- Assumes standard conditions: 1 M concentration, 1 atm pressure, 25°C temperature

Real-World Conditions: The Nernst Equation

When conditions deviate from standard, the **Nernst equation** is used to calculate the actual cell voltage, $E= E_{cell}^\circ- (RT/nF)\ln Q$

Where: R: Gas constant (8.314 J/mol·K),T: Temperature in Kelvin, n: Number of moles of electrons transferred, F: Faraday's constant (96485 C/mol) and Q: Reaction quotient (ratio of product to reactant concentrations)

This equation shows how concentration and temperature affect cell voltage.

Thermodynamic Perspective

Voltage is also linked to the **Gibbs free energy** change ΔG:

$\Delta G= - nFE$

A negative ΔG indicates a spontaneous reaction.

- This equation connects electrochemical energy to chemical thermodynamics.

Example Calculation

For a Zn–Cu cell: $E_{Zn} = - 0.76V$, $E_{Cu} = + 0.34$ V

- $E_{cell}^o = 0.34-(-0.76) = 1.10$ V = 0.34 - (-0.76) = 1.10 V

This voltage reflects the energy released when electrons flow from Zn to Cu^{2+} ions.

IIE. What is the formula for calculating the standard cell voltage E_{cell}° ?

The formula for calculating the standard cell voltage E_{cell}° is given by the following:

$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$

$E_{cell}^\circ = E_{cathode}^\circ \times E_{anode}^\circ$

$E_{cell}^\circ = E_{anode}^\circ - E_{cathode}^\circ$

$E_{cell}^\circ = E_{cathode}^\circ + E_{anode}^\circ$

Where, E_{cell}° = Cell potential at standard state condition.

= $E_{cathode}^\circ$ = Cathode potential at standard state condition.

E_{anode}^{o} = Anode potential at standard state condition.

IV. Conclusions

Electrochemical conversion of carbon dioxide (CO_2) into value - added products presents a promising route toward sustainable energy solutions. This study investigates the role of voltage regulation in enhancing the performance of silver nanoparticles (AgNPs) as electrocatalysts for CO_2 reduction. Voltage-dependent analysis reveals that AgNPs exhibit optimal CO production and Faradaic efficiency near -1.6 V vs. RHE, with selectivity for CO peaking below -1.1 V due to favorable *COOH intermediate formation and suppressed hydrogen evolution. Surface coverage of key intermediates such as $*CO_2^-$, *COOH, and *CO demonstrates strong voltage sensitivity, influencing reaction pathways and product distribution. Ligand-free AgNPs, particularly in the 10 -30 nm size range, outperform bulk silver, offering enhanced catalytic activity and selectivity. The resulting H_2:CO ratio (~2.9:1) is well-suited for syngas applications, underscoring the potential of AgNP-based systems in carbon-neutral fuel production.

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