Catalyst-free oxalate production in water from CO_2 discharge: Modelling perspectives

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Abstract: This study demonstrates high-performance, catalyst-free conversion of CO_2 and water into hydrogen peroxide ($H_2O_{2(aq)}$) and oxalate ($C_2O_{4(aq)}^{2-}$) using CO_2-pulsed spark discharge through microbubbles. Our plasma chemistry modelling highlights the role of high-density electrons and $C_xO_y^+$ ions at the bubble interface in driving efficient oxalate production. The contribution of vibrationally excited $CO_2(v)$ will also be discussed.

1. Introduction

The notable rise in atmospheric CO_2 since the mid-18th century has escalated global challenges, making the urgent development of carbon capture, utilization, and storage (CCUS) technologies essential to achieve net-zero emissions [1]. Considerable progress has been made in CO_2 reduction to C1 chemicals, but converting CO_2 to valuable multicarbon (C2+) products like oxalic acid remains challenging, with faradaic efficiency (FE) typically under 60% in aqueous systems [2]. Plasma-enabled CO_2 reduction has shown promise for producing oxalate and formic acid, but it suffers from limited reactive regions and high energy demands. A catalyst-free, microbubble-enhanced plasma-electrified system addresses these issues, using water as a sustainable reducing agent and enabling efficient, simultaneous production of oxalic acid and hydrogen peroxide, a valuable co-product for green chemical production [3].

2. Methods

Our CO_2-H_2O plasma model incorporates electron kinetics in the gas phase, including ionization, excitation, and recombination, based on an established CO_2-related model [4]. The spark discharge condition was set with input parameters of E/N = 40 Td and an exponentially decaying electron density profile, peaking at 4.2×10^{13} cm^{-3}, estimated from voltage-current characteristics. An aqueous phase model was then developed to support enhanced oxalate formation over formate ($HCO_{2(aq)}^-$) by adapting the concept of formate coupling.[5]

3. Results

The modelling results confirm that for $H_2O_{2(aq)}$ production, OH, a critical precursor, is primarily formed by the dissociation of H_2O via electrons in the spark discharge near the water interface. H_2O_2, with its high Henry's constant (1.92×10^6), efficiently transfers from the gas phase to the liquid phase as $H_2O_{2(aq)}$, where its density further increases with contributions from $HO_{2(aq)}$. Initially, formate dominates over oxalate in water through interactions between $CO_{2(aq)}^-$ and $H_2O_{(aq)}$, but oxalate steadily grows via formate coupling ($HCO_{2(aq)}^- + HCO_{2(aq)}^- \rightarrow C_2O_{4(aq)}^{2-} + H_2$), eventually surpassing formate and saturating at higher concentrations, consistent with experimental observations. Additionally, ionic species such as CO_2^+ and $C_xO_y^+$ play a critical role in increasing $CO_{(aq)}$ and $CO_{2(aq)}$ densities in water.

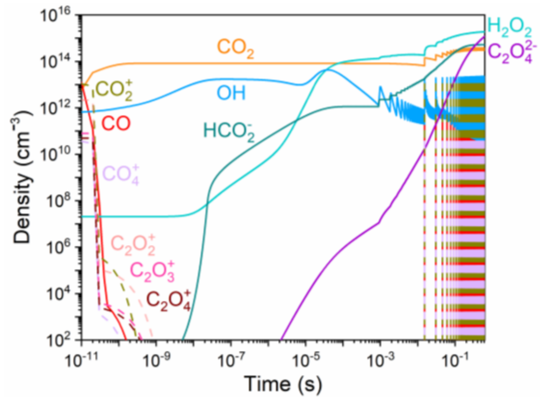

Fig. 1. Density profiles of important aqueous phase species from CO_2 spark discharge with 2 vol.% of H_2O at E/N = 40 Td, peak $n_e = 4.2\times10^{13}$ cm^{-3}.

4. Summary and Discussion

Spark discharges initiate high-density CO_2(aq) formation in water, driving efficient production of formate and oxalate. While the model highlights the role of ions and excited species in increasing CO_2(aq) density, it underestimates production rates when vibrationally excited $CO_2(v)$ is excluded. The impact of $CO_2(v)$ on these reactions will be considered.

References

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