Modeling chemical reactions in contact glow discharge electrolysis

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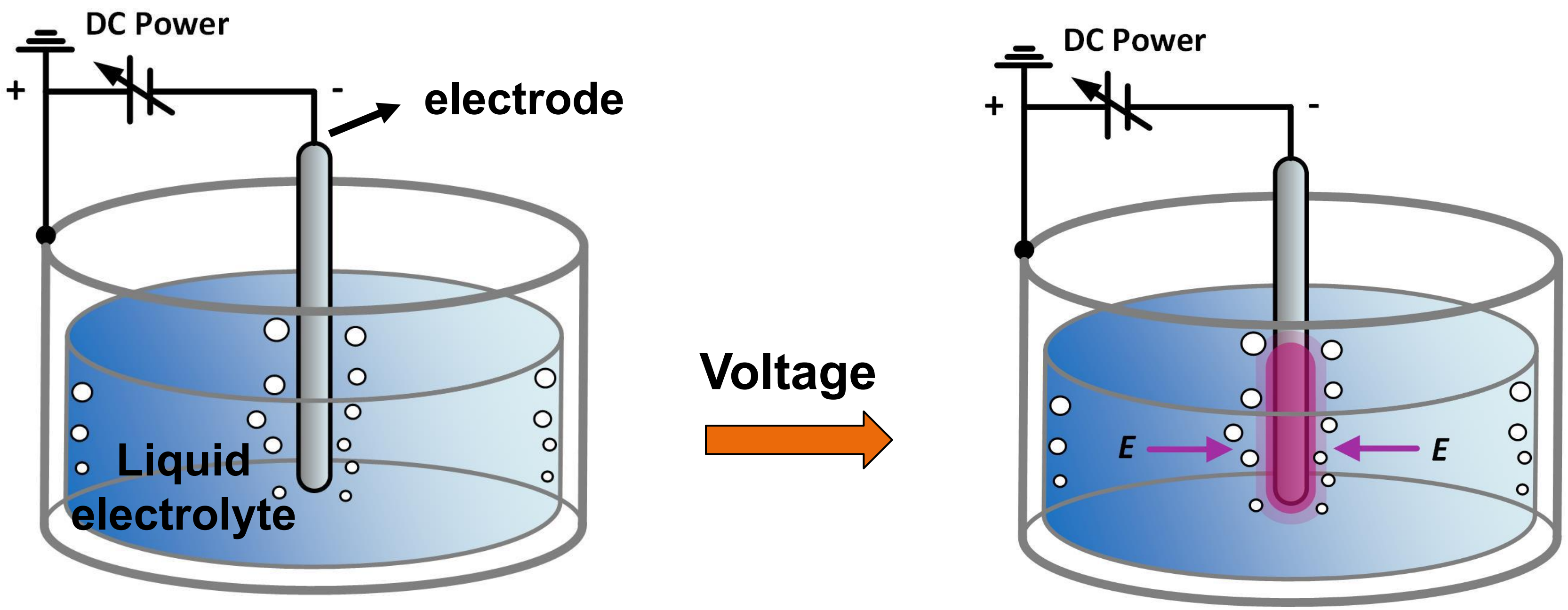
Contact glow discharge electrolysis

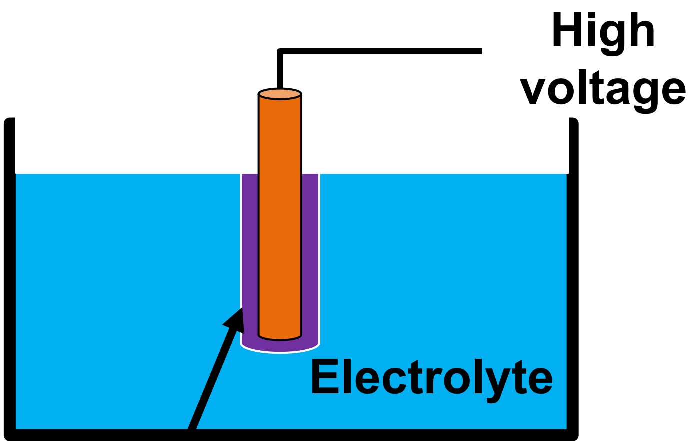
- What is contact glow discharge electrolysis (CGDE)?
  - also called “plasma electrolysis” = electrolysis + plasma discharge



Normal electrolysis

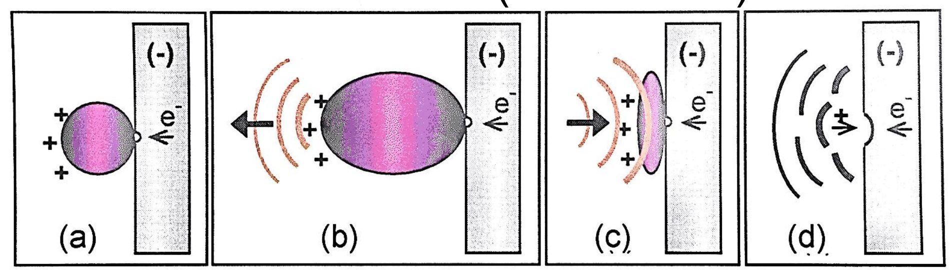
Contact glow discharge electrolysis

Physical-processes-dominated discharge



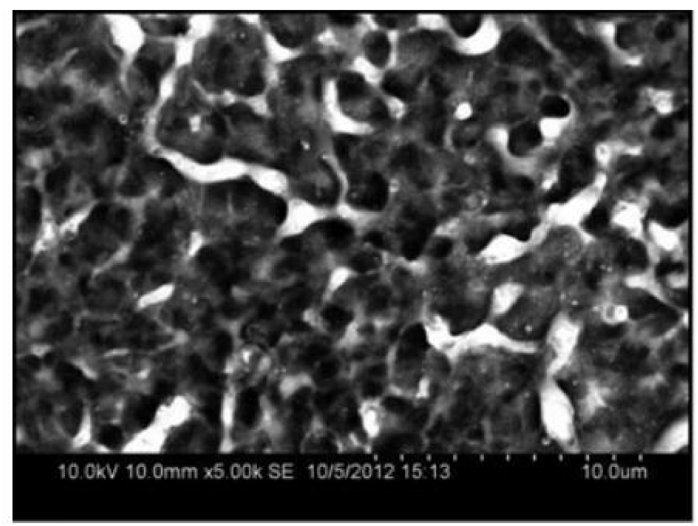
Vapor layer induced by Joule heating:
High resistance
Large potential drop

Physical processes + chemical reactions (dominated)

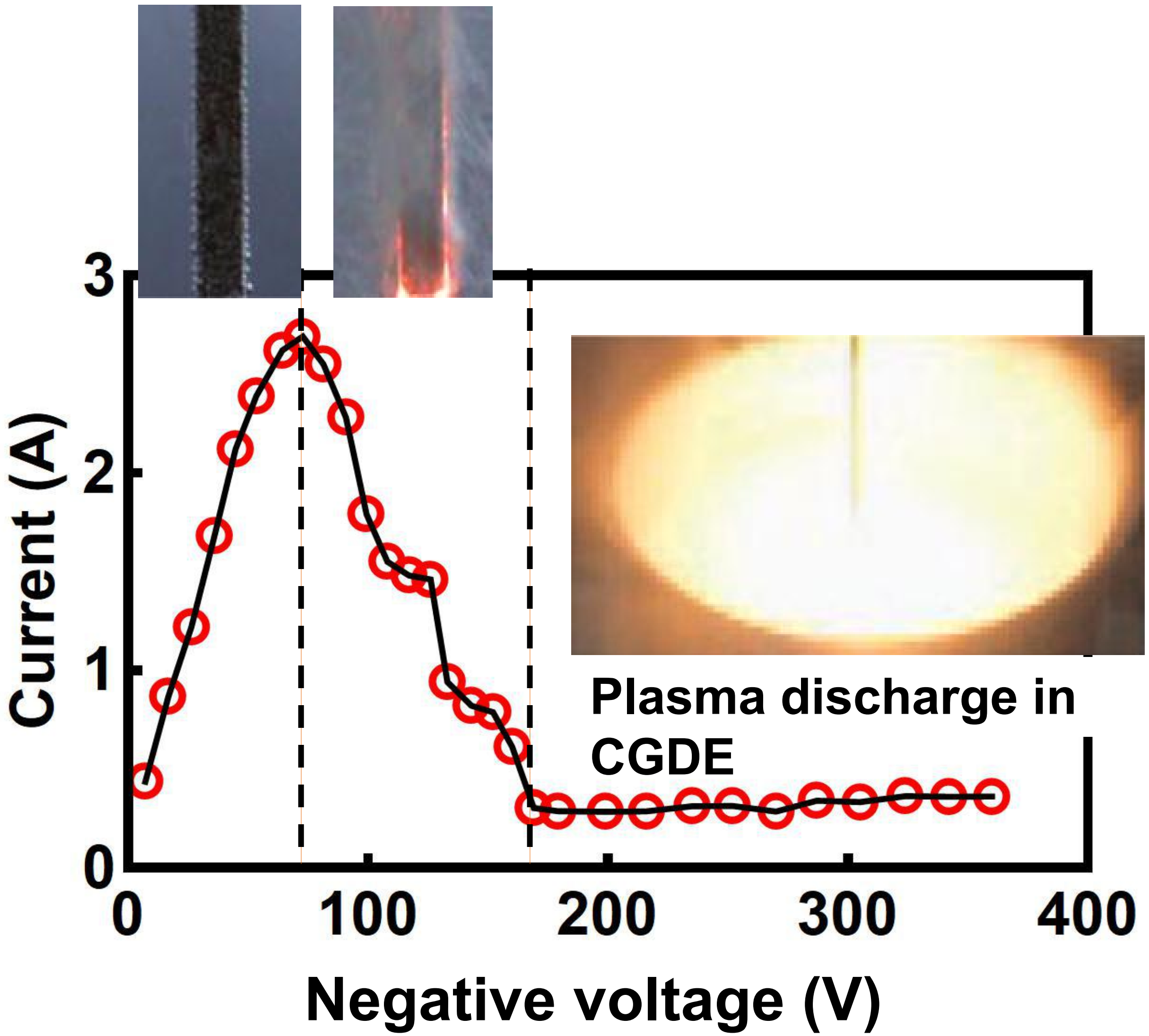


Physical process in PE. (a) Plasma formation around cathode, (b) plasma expansion and induction of shock wave, (c) collapse of plasma bubble due to electrolyte quench, and (d) explosive impact on electrode surface.

Large (100 nm ~ 2 um) and nonuniform particles + irregular porous morphology



Typical I-V curve of CGDE



Decoupling of physical processes and chemical rea

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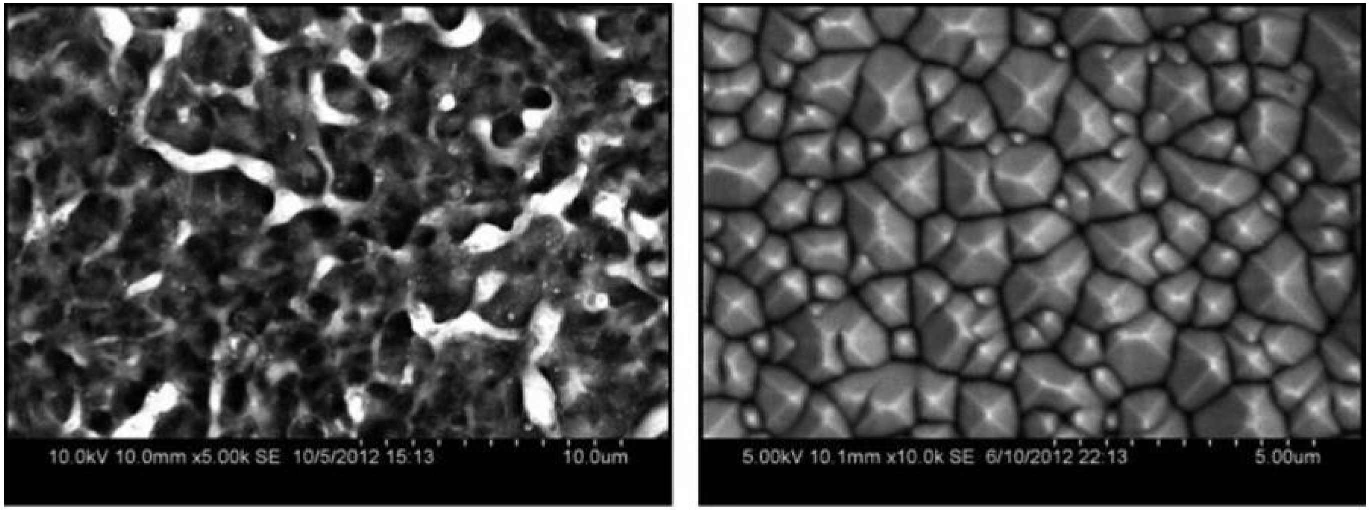
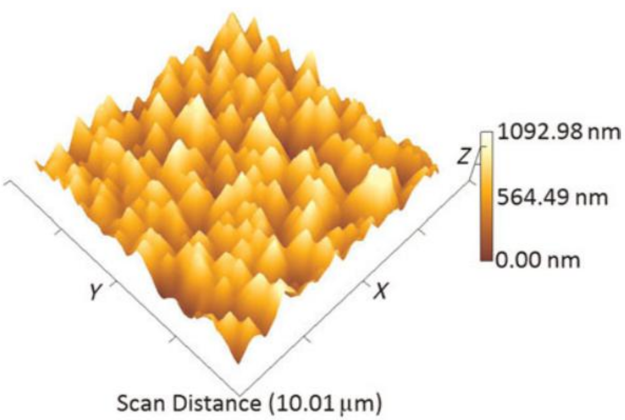


(a) (b)

(a) Porous and (b) textured Si wafer obtained by PE using electrolyte with **glycerol : water** ratios of (a) 5:1 and (b) 10:1. In both cases, a mirror-polished Si wafer was used as cathode.

Si nanoparticles of ~80 nm size created by CGDE.



Textured surface and nano-particles can only be created by anisotropic chemical etching: Decoupling of physical processes and chemical reactions

Mechanisms of decoupling

Properties of water and glycerol at 293 K.

	Surface tension (mN/m)	Density (g/cm^3)	Viscosity (mPa·s)	Boiling point
Water	72.80	0.998	1.002	373 K
Glycerol	64.00	1.261	1412	563 K

beneficial for the formation of a continuous and stable vapor layer

Reduce the generation of gas bubbles & localized intensive physical interactions

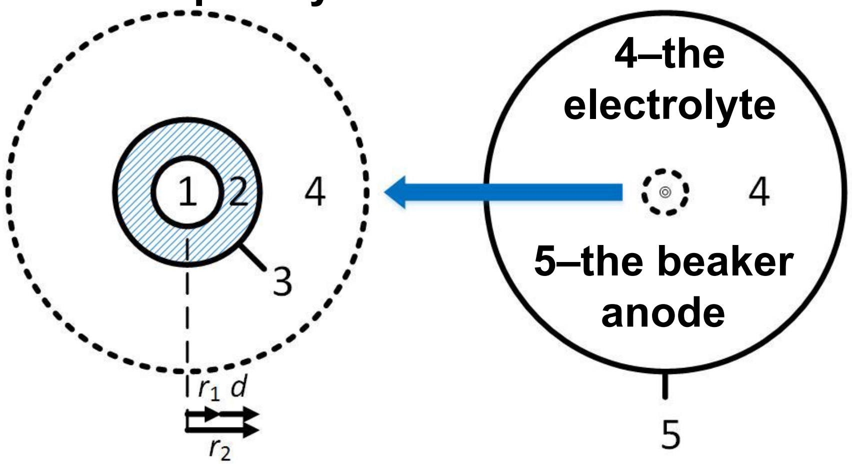
suppress the physical processes, e.g., bubble implosion, shock wave, stabilize the vapor layer

Model description

- Further understanding of the plasma-liquid interactions requires modeling
- The difficulty for detailed modeling: Complicated physical and chemical reactions
- Decoupling: only simulate the chemical reactions in CGDE

1–the wire cathode

2–the vapor layer



3–the plasma-liquid interface

Top-view of discharge

Simplified as 1D cylindrical coordinate

29 species and 84 reactions

Species considered in the cathodic plasma electrolysis model.

Species	Neutral	Positive	Negative
H-species	H, H_2, H(2p), H(2s)	H^+, H_2^+, H_3^+	H^-
O-species	O, O_2, O_3, O_2(a)	O^+, O_2^+	O^-, O_2^-, O_3^-
OH-species	OH, H_2O, HO_2, H_2O_2	OH^+, H_2O^+, H_3O^+	OH^-
Water clusters		$H_2O_3^+$, $H_4O_2^+$, $H_5O_2^+$	
Others			e

Model description

- Continuity equation
  - For each species except water

$$\frac{\partial n_j}{\partial t} + \nabla \cdot \boldsymbol{\Gamma}_j = R_j - \boxed{k_{\mathrm{loss}} n_j}$$

- Drift-diffusion approximation

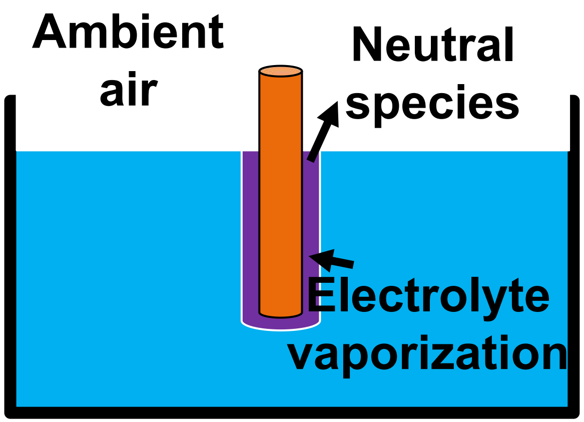
$$\boldsymbol{\Gamma}_j = z_j \mu_j n_j \boldsymbol{E} - \nabla (D_j n_j)$$

- Energy conservation equation

$$\frac{\partial n_\varepsilon}{\partial t} + \nabla \cdot \boldsymbol{\Gamma}_\varepsilon + \boldsymbol{E} \cdot \boldsymbol{\Gamma}_{\mathrm{e}} = Q$$

- Poisson's equation

$$\nabla^2 \varphi = \frac{e}{\varepsilon_0} \left(\sum_i n_i - n_{\mathrm{e}} \right)$$



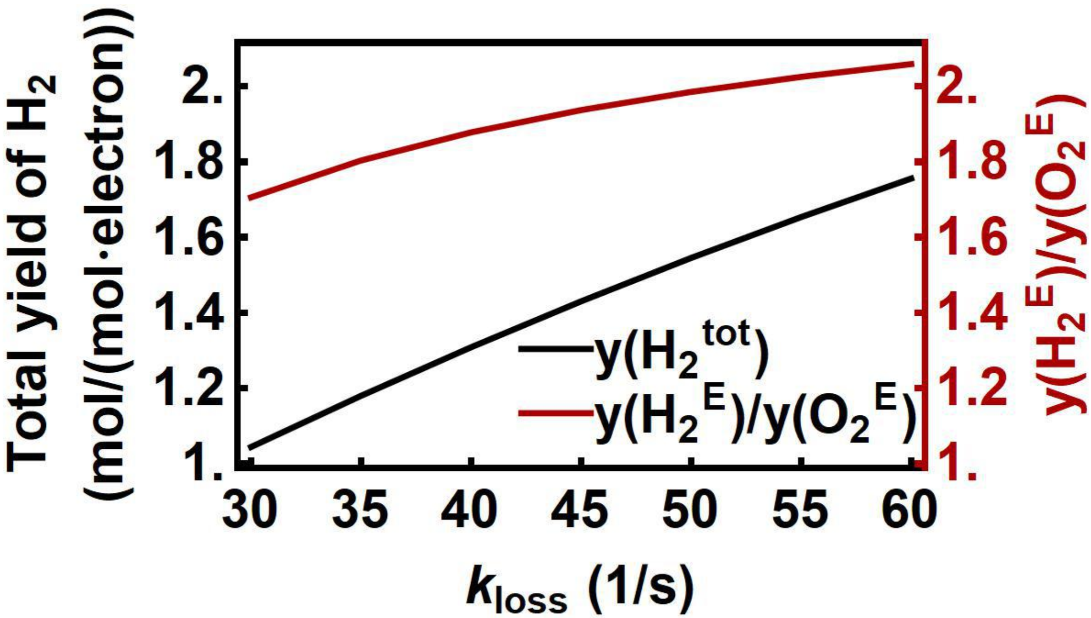
Discharge system is not closed

H_2O number density

$$n_{\mathrm{H_2O}} = n_{\mathrm{tot}} - \sum_{j \neq \mathrm{H_2O}} n_j$$

Loss rate coefficient

- Fit k_{loss} with experimentally measured gas yields
- From Faraday's law $R_{H_2} = \frac{J_d}{2eN_A d}$
- faradaic yield of H_2: $y(H_2) = 0.5\,\text{mol/(mol·electron)}$
- Total chemical yield of H_2: $y(H_2^{tot}) = \frac{R_{H_2}^{tot}}{R_{H_2}} \cdot y(H_2)$ $\quad R_{H_2}^{tot} = c_{H_2} k_{loss}$
- Non-faradaic yield of H_2 and O_2: $y(H_2^E) = y(H_2^{tot}) - y(H_2)$ $\quad y(O_2^E) = \frac{c_{O_2} k_{loss}}{R_{H_2}} \cdot y(H_2)$



Experimental results

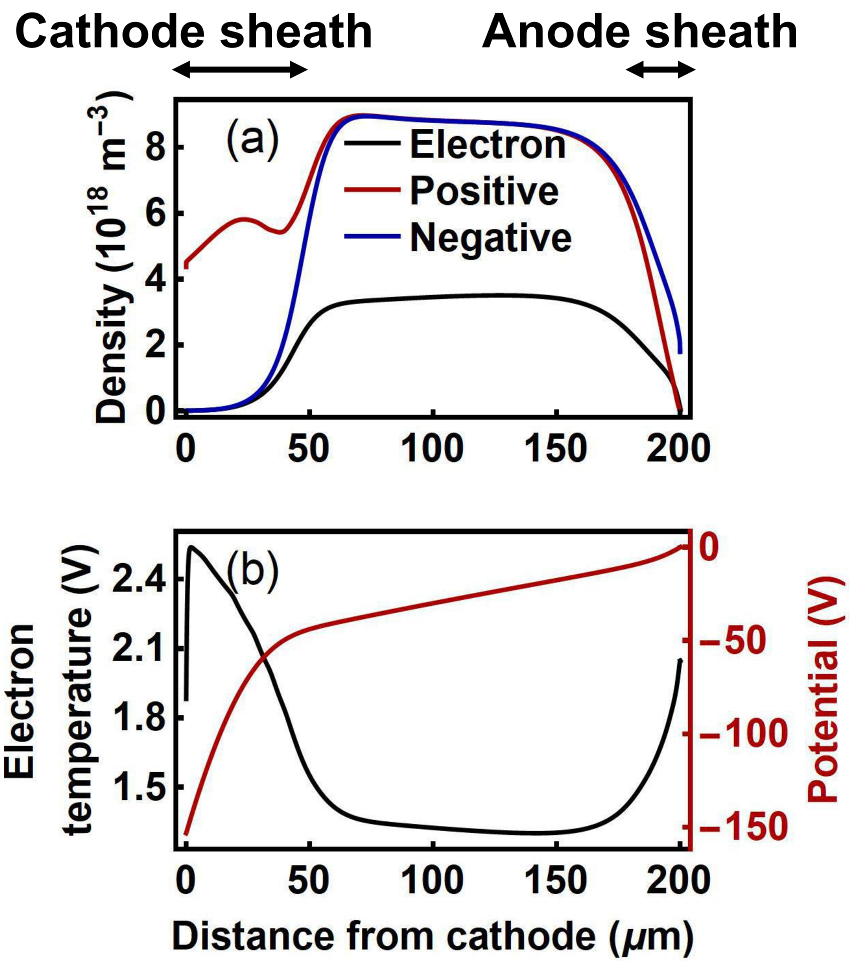
$y(H_2^E)/y(O_2^E) \approx 2$

$y(H_2^{tot}) = 1.0\text{–}1.5\,\text{mol/(mol·electron)}$

Estimated k_{loss} of 45 s^{-1}

Base case simulation

- Highly electronegative plasma

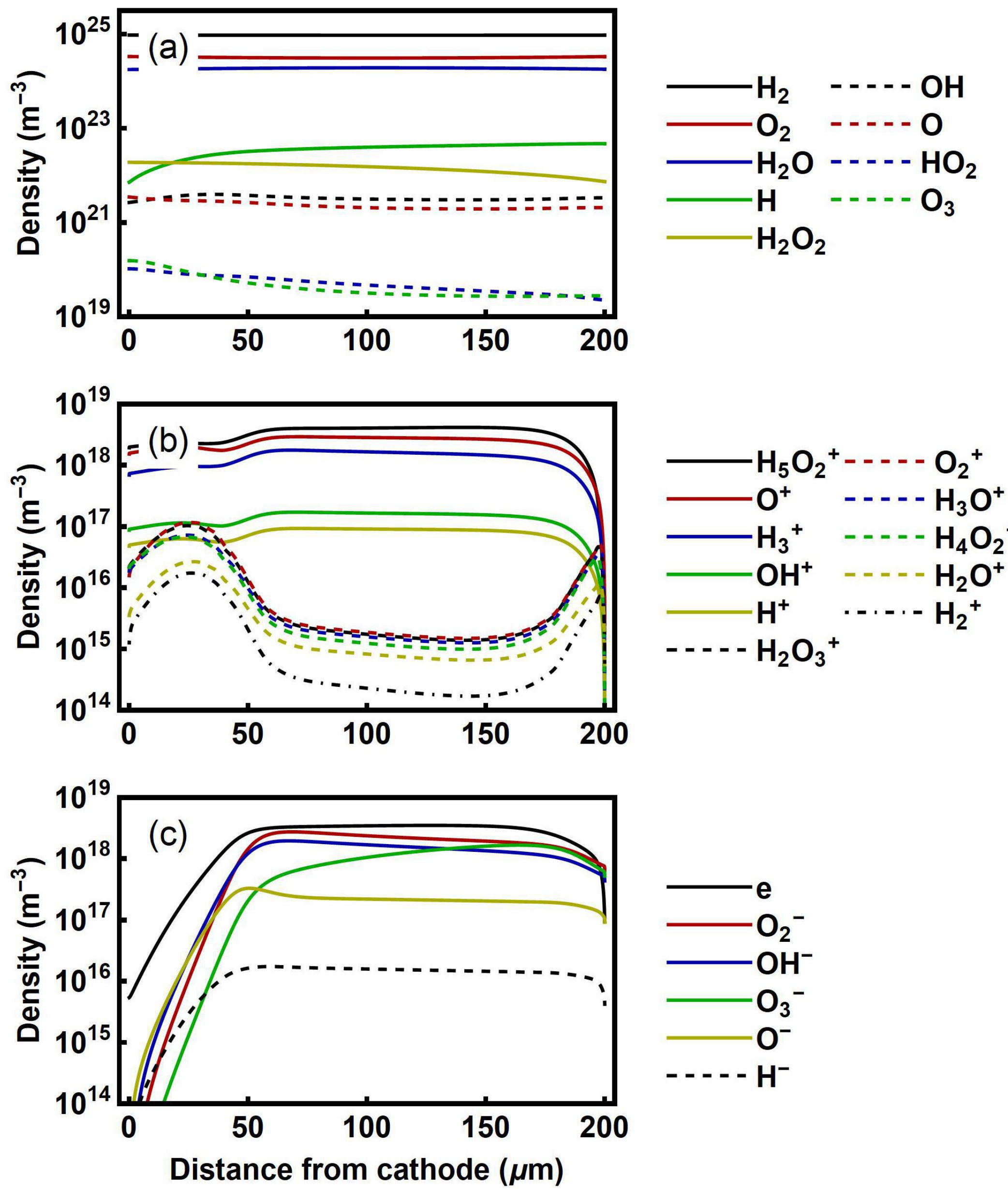


Input parameters for a base case simulation of cathodic PE discharge.

Parameter	Value	Description
p	1 atm	Pressure
l	5 mm	Cathode length immersed in the liquid
r_1	1 mm	Cathode wire radius
V_d	250 V	Discharge voltage
I_d	0.3 A	Discharge current
R_b	250 Ω	Ballast resistance
d	200 μm	Vapor layer thickness
T_g	500 K	Vapor layer temperature
k_{loss}	45 s^{-1}	Loss rate of neutral species
$\gamma_{H_2O_2}$	0.01	Sticking coefficient of H_2O_2 at the liquid anode
γ_H	1	γ_α
γ_O	1	γ_α
γ_{OH}	1	γ_α
γ_m	1	γ_α for de-excitation at the electrode surface
$\gamma_{e,c}$, $\gamma_{e,a}$	1	γ_e of electrons at the cathode or anode
γ_ε	1	Sticking coefficient for electron energy
$r_{i,p,c}$	0	r_i of positive ions at the cathode
$r_{i,p,a}$	1	r_i of positive ions at the anode
$r_{i,n,c}$	1	r_i of negative ions at the cathode
$r_{i,n,a}$	0	r_i of negative ions at the anode

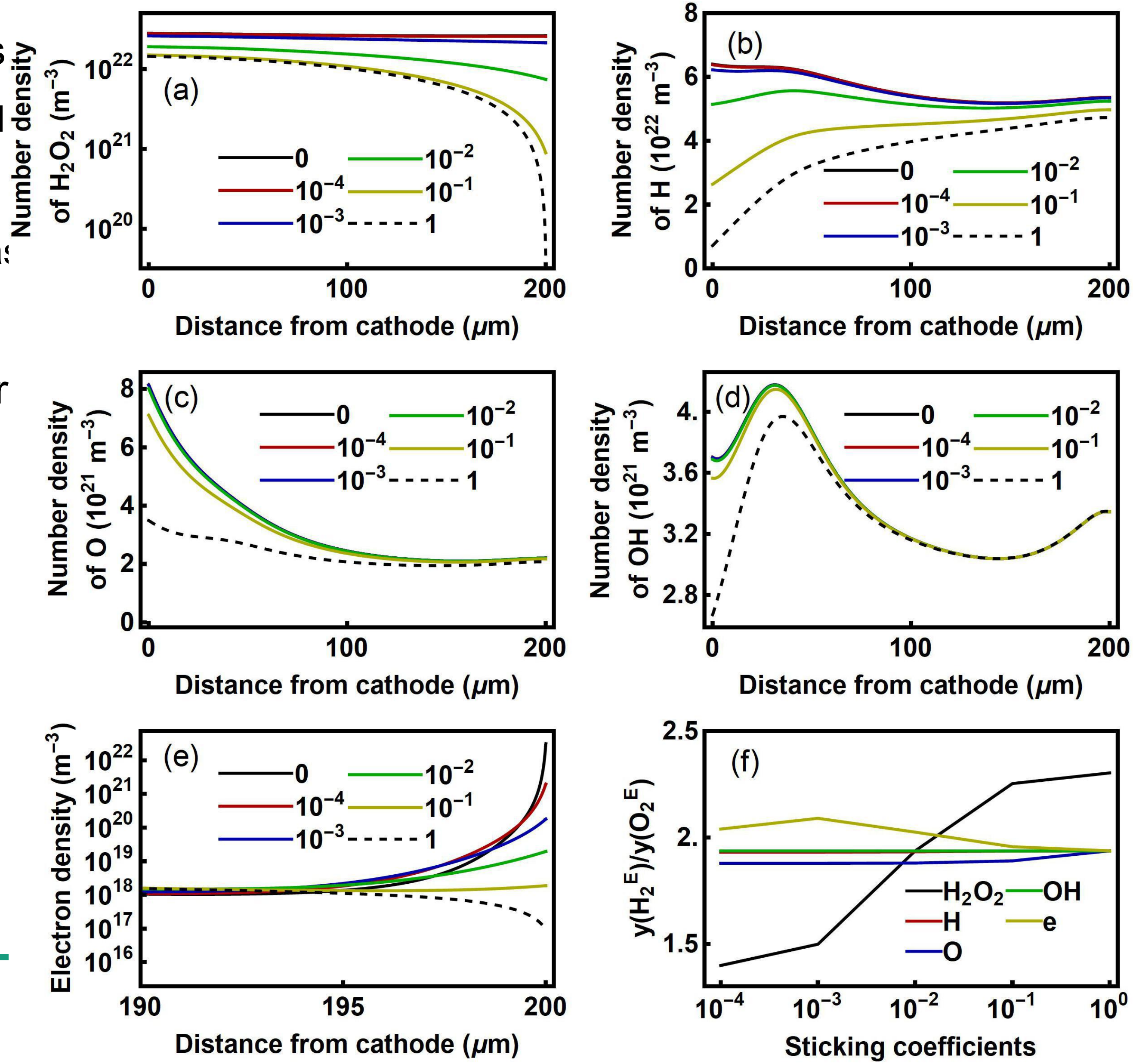
Number densities

- Primary neutral species
  - H_2, O_2
  - $n_{H2}/n_{O2} \approx 2$
  - Dissociation degree of H_2 and O_2 < 1%
- Primary positive ions
  - $H_5O_2^+$, O^+, H_3^+
- Primary negative ions
  - O_2^-, O^-, O_3^-, OH^-



Influence of undetermined parameters

- Boundary conditions
  - Lack of fundamental data for particle-surface reaction in atmospheric plasmas
- Influence of boundary conditions
  - Change the sticking coefficient for each species
  - Only the change of H_2O_2 is significant
  - Fitting the sticking coefficient of H_2O_2 with experimental results



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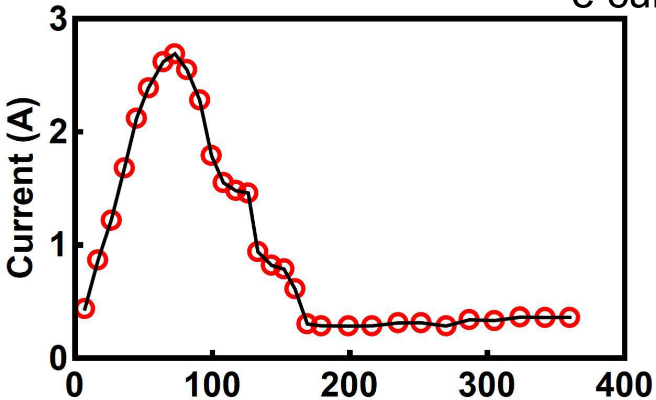
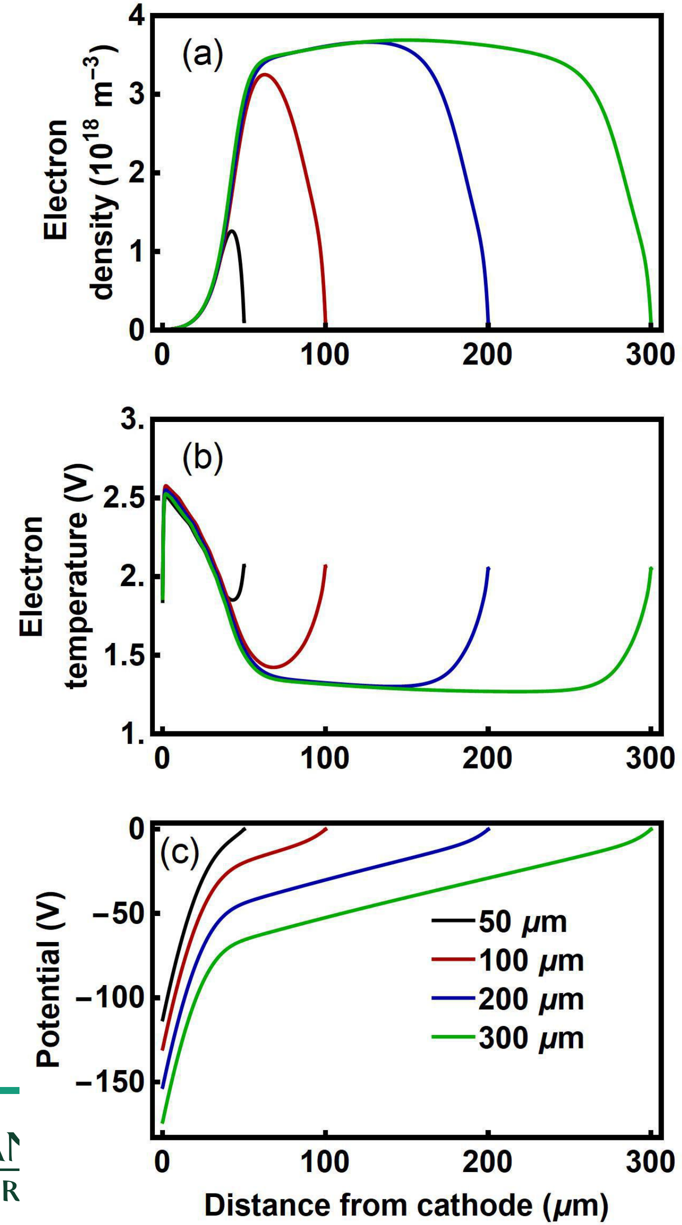
Influence of vapor layer thickness

- Vapor layer thickness
  - Dozens to hundreds of um
  - Determined by the thermal energy gain and loss
- A fully developed discharge requires a vapor layer thickness greater than 100 um

Discharge voltage $V_d = V_p + R_b \cdot I_d$ Potential drop in the plasma, Ballast resistance, Discharge current

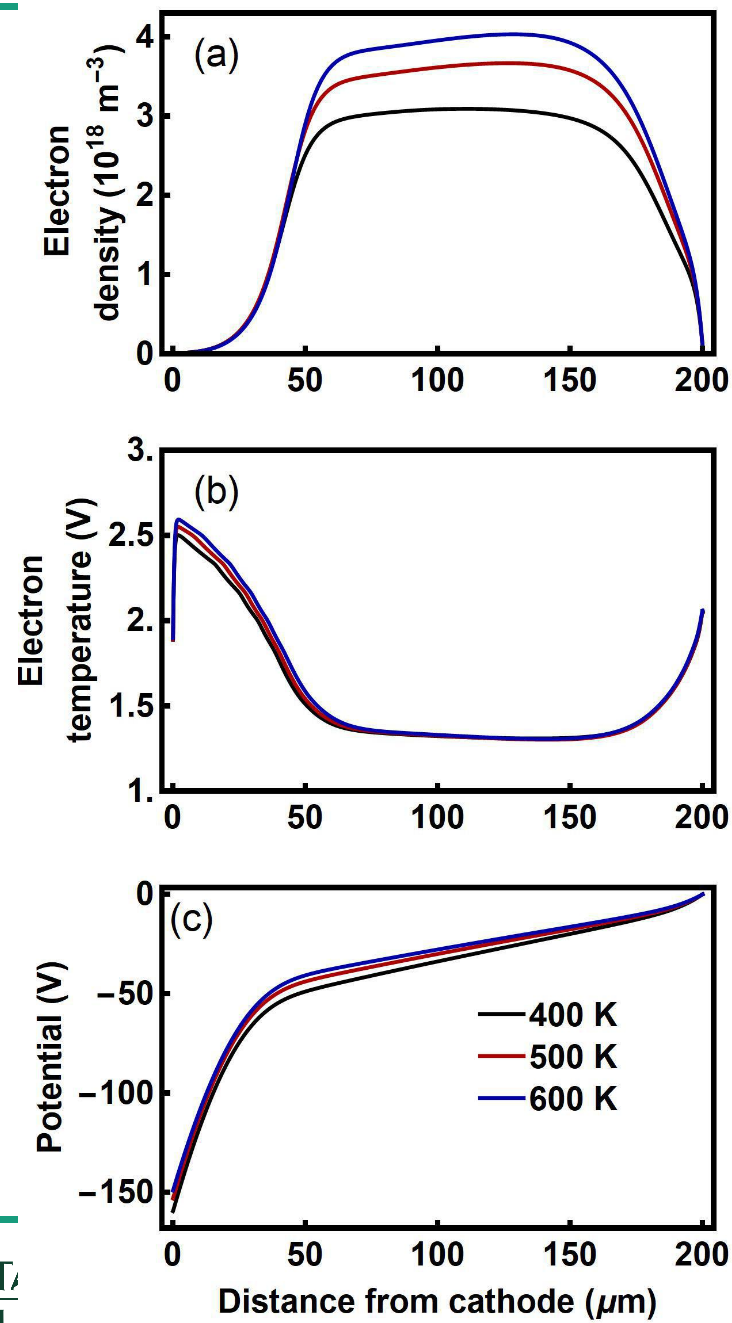




Influence of gas temperature

- As increasing the gas temperature
  - Electron density slightly increases
  - Electron temperature & electric potential
    are barely influenced

- The fluctuation of temperature in this range
  has no significant influence on the discharge



Conclusions

- It has been found that with the increase of **glycerol/water ratio** in the electrolyte, the physical processes and the chemical reactions could be **decoupled.** A **textured electrode surface** and a **uniform nanoparticle size distribution** can be created through a **chemical-reaction-dominated** process instead of an irregular porous surface and a large and nonuniform distribution produced by the physical-reaction-dominated interactions. The formation of a textured surface is attributed to the anisotropic chemical etching on the silicon electrode by the reactive species generated in the plasmas.
- The cathodic plasma electrolysis discharge process is investigated using a **one-dimensional plasma fluid model** with constraint conditions obtained from the experiments. The model is developed under the conditions when the physical interactions between the plasma and the working electrode is suppressed, and the discharge is **chemical-reaction-dominated**. The modeling results demonstrate a high plasma density on the order of 10^{19} m^3 and a low electron temperature of about 1.2-1.3 V in the bulk plasma region. The plasma is highly **electronegative**, and the dominant neutral species are H_2 and O_2 dissociated from water vapor. A linear relationship between the discharge voltage and the vapor layer thickness is predicted in the stable discharge region, due to the high Joule heating from the working electrode. A vapor layer thickness greater **100 um** is required to obtain a fully developed discharge. The fluctuation of gas temperature has **no great influence** on the discharge process.

Thank you

for your

attention