Plasma-Chemical Reactions Governed by the Specific Energy Input – Plasma Polymerization and Beyond

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Abstract: Molecular gases in low temperature plasmas undergo many inelastic collisions since the activation barrier for excitation and dissociation is lower than their ionization energy. Tayloring the specific energy input with respect to the activation barrier of a specific plasma-chemical reaction can be used to optimize plasma polymer films regarding deposition rate and functionality. Similarly, plasma gas conversion can be addressed to evaluate energy efficiency.

Keywords: energy input, plasma polymer films, plasma conversion, energy efficiency

1. Introduction

A low temperature plasma, that is, a weakly ionized gas, provides highly non-equilibrium conditions, meaning that the light particles, the electrons, pick up energy from the electric field in collisions with the heavy particles, the gaseous atoms and molecules. While the latter might remain close to room temperature, the electrons gain high kinetic energies that must be sufficient for ionizing reactions to sustain the plasma. For molecular gases, an average energy per heavy gas particle is thus available in the plasma, known as specific energy input (SEI), yielding plasma chemical reactions by inelastic collisions (excitation, dissociation, and ionization). Since the mean free path lengths for such activation reactions follow a distribution law, the probability for the activation mechanism can be described by a simple Arrhenius-like equation, where temperature is replaced by SEI. The potential of this approach is demonstrated on the basis of plasma polymerization of siloxane and hydrocarbon thin films (and others) as well as plasma CO_2 conversion.

2. Plasma chemical reactions

In noble gases, excitation reactions are activated by direct electron impact collisions, since the activation barrier to generate, for example, Ar metastables is rather high (~11.5 eV). Thus only electrons with impact energies above this threshold energy, E_{th}, yield inelastic collisions (**Figure 1**). In molecular gases, on the contrary, excitation occurs with high cross sections already for low energies. Exemplarily, the total cross section for CO_2 excitation is displayed in **Figure 1**. While CO_2 dissociation by electron impact collisions is observed above 7 eV, intermediates such as vibrationally excited states are populated at much lower energies promoting the reaction at reduced energies. Plasma chemical reactions in molecular gases thus proceed efficiently via intermediates.

To address this situation, it is convenient to use the energy available per molecule in the plasma, E_{pl}, as governing parameter:

$$E_{pl} = \frac{k_B T_0}{p_0} \frac{W_{abs}}{F_m} \tag{1}$$

The specific energy input (SEI) is thus related to macroscopic parameters, absorbed power, W_{abs}, per molecular gas flow rate, F_m, in the plasma volume using Boltzmann constant, k_B, temperature, T_0, and pressure, p_0, at standard conditions. The energy density, power per flow rate, is thus transferred to an energy per molecule (in [eV]).

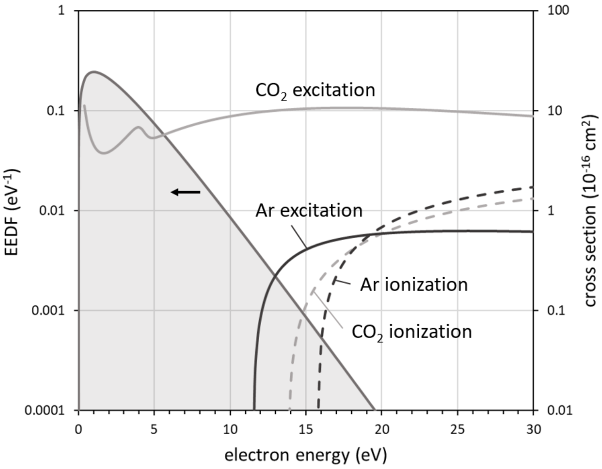

Fig. 1. EEDF for $T_e = 2$ eV and total excitation and ionization cross sections for Ar and CO_2. Anlytical expressions are used to plot the cross sections as taken from literature [1, 2].

Considering that SEI is following a distribution law (Boltzmann's energy distribution), the probability that plasma activation with the threshold energy, E_{th}, occurs is given by an Arrhenius-like form, which holds for $E_{pl} \geq E_{th}$:

$$v_{in} = v_{in,0}\, exp\left(-\frac{E_{th}}{E_{pl}}\right) \tag{2}$$

Here, v_{in} is the observed reaction rate for inelastic collisions. The pre-exponential factor, $v_{in,0}$ can be seen as the ideal rate for plasma activation if either E_{th} would be zero, or if E_{pl} would exceed E_{th} in a way that all molecules react.

Assuming a simple rate equation for plasma activation, the reaction rate can directly be related to the conversion of the starting molecule into a product [3]. In plasma polymerization, the conversion results in a deposit, the plasma polymer film, while gaseous products are examined in plasma gas conversion.

For $E_{pl} \leq E_{th}$, intermediates with $E_{th,i} < E_{th}$ are populated by electron impact collisions allowing a conversion that is linearly increasing with E_{pl}/E_{th} [3]. The plasma chemical conversion of the reactant into the activated product, c_a, with respect to the maximum conversion, c_0, for a given experimental set-up (e.g. $c_0 = 1$ for optimum conditions) can thus be expressed as

$$\frac{c_a}{c_0} = \begin{cases} \alpha_0 \frac{E_{pl}}{E_{th}}, \, E_{pl} \leq E_{th} \\ exp\left(-\frac{E_{th}}{E_{pl}}\right), E_{pl} \geq E_{th} \end{cases} \tag{3}$$

with $\alpha_0 = exp(-1)$, and $\alpha = \alpha_0 \cdot c_0$ being the conversion at $E_{pl} = E_{th}$, which is thus limited to 36.8%.

3. Plasma polymerization

In plasma polymerization it is convenient to assess the conversion of the used monomer into film-forming species by measuring deposition rates. The dimensionless effective conversion into the deposit, c_{dep}, is given by the mass deposition rate, R_m, normalized by monomer flow rate, F_m, deposition area, A_{dep}, and the mass of the deposited species, M_{dep}, which is related to the fraction of activated molecules, c_a, by

$$c_{dep} = R_m \frac{A_{dep}}{F_m} \frac{N_A}{M_{mol}} \frac{k_B T_0}{p_0} = s \, \frac{M_{dep}}{M_{mol}} \, c_a \tag{4}$$

with Avogadro's number, N_A [3]. Furthermore, the molecular mass of the depositing species, M_{dep}, and their sticking probability, s, needs to be considered. Note that c_{dep} is thus smaller than the actual conversion in the gas phase. This method is most suited for plasma state polymerization, that is, when gas phase processes determine the deposition rate (and not ion bombardment). Hexamethyldisiloxane is an example for a model monomer following Arrhenius-like behaviour, from which the plasma-chemical reaction mechanism was examined revealing intermediates such as vibrationally excited states, methyl group abstraction and opening of the Si–O bond yielding highly reactive O–Si–CH_2 biradicals as film-forming species ($s \approx 1$) [3]. For example, the deposition of hydrophobic silicone-like films can thus be optimized. Remarkably, the remaining species, Si–$CH_{2/3}$, with lower sticking probability also contribute to deposition in cavities and undercuts. This effect is further investigated for the functionalization of complex geometries such as textiles and scaffolds.

The comparison of different hydrocarbons as monomers in the plasma allows to discuss their reaction pathways and sticking probabilities. Acetylene, C_2H_2, forms highly reactive C_2H radicals that have been reported to have $s \approx 0.8$ [4]. Film growth thus follows Arrhenius-like behaviour according to Eq. (3) and (4) as depicted in **Figure 2**. Ethylene, C_2H_4, also reveals a linear increasing conversion up to $E_{th} \approx 10$ eV followed by Arrhenius-like behaviour, however, with reduced deposition rate (conversion into deposit) indicating a lower reactivity. Indeed, a lower $s \approx 0.25$ has been reported considering C_2H_3 as film-forming species [4]. With increasing SEI, that is, E_{pl}, on the contrary, a deflection towards higher deposition rates is observed. It can thus be assumed that stronger H abstraction results in the same film-forming species as for C_2H_2, approaching its deposition rate. This is known as 'lost memory effect' – with sufficient energy input film properties resemble one another independent of the used starting hydrocarbon monomer. The plasma chemical reaction pathway thus involves multistep reactions.

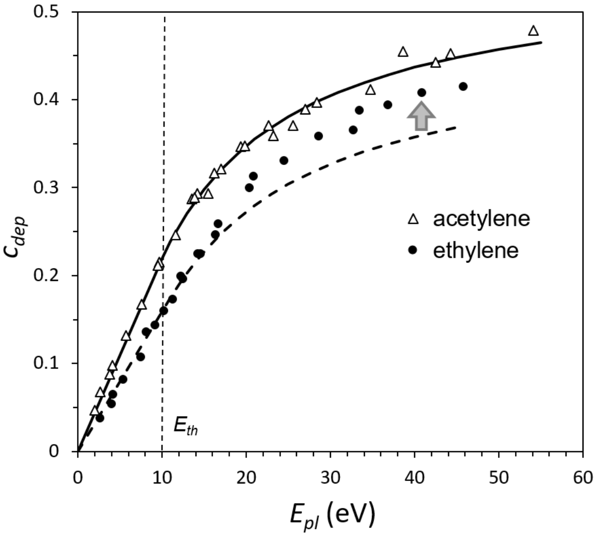

Fig. 2. Conversion into film growth for C_2H_2 and C_2H_4 in a symmetric CCP RF plasma at 7 Pa. The deflection from the Arrhenius curve for C_2H_4 at increasing SEI indicates the formation of more reactive species.

Moreover, it has been demonstrated that many more monomers as used for plasma polymerization follow this Arrhenius-like behaviour, including hydrocarbons, fluorocarbons, siloxanes, silanes, organic monomers, and mixtures with non-polymerizable gases [5]. Process optimization, scaling, and implementation in industry are thus largely facilitated.

4. Plasma CO_2 conversion

For CO_2 conversion yielding CO + ½ O_2, energy efficiencies are a key factor. Since the energy efficiency, η, is defined as

$$\eta = c_a \frac{\Delta H}{E_{pl}} = c_0 \begin{cases} \alpha_0, \, E_{pl} \leq E_{th} \\ \frac{E_{th}}{E_{pl}} exp\left(-\frac{E_{th}}{E_{pl}}\right), E_{pl} \geq E_{th} \end{cases} \tag{5}$$

with $\Delta H = E_{th} = 2.9$ eV for CO_2 conversion, the efficiency can be assessed depending on E_{pl}/E_{th} assuming Arrhenius-like behavior regarding Eq. (3), as given in the right hand side of Eq. (5). Note that the reaction at the enthalpy of CO_2 dissociation is assumed to occur in a plasma when the plasma-chemical reaction pathway involves many vibrationally excited states, CO_2*, with small energy gaps and collisions among them, so-called 'ladder climbing', allowing dissociation at the C–O bond energy of 5.5 eV as well as the further conversion via the generated side product, atomic oxygen, with CO_2 at 0.3 eV, resulting in the overall threshold energy of about 2.9 eV [6]. The energy efficiency in Eq. (5) can be expressed as a function of conversion, yielding for $E_{pl} \geq E_{th}$:

$$\frac{\eta}{c_0} = -\frac{c_a}{c_0}\, ln\left(\frac{c_a}{c_0}\right) \tag{6}$$

This $-x \cdot ln\, x$ function, e.g. known as entropy term, has a maximum at $E_{pl} = E_{th}$, where $\eta = c_a = \alpha$, which might be named 'alpha point'. For $E_{pl} \leq E_{th}$, however, intermediates allow enhanced conversion resulting in a constant energy efficiency, as discussed for plasma polymerization [7]. The ladder climbing mechanism further involves collisions among excited molecules beside electron impact collisions, which can enhance the conversion and thus the efficiency even more at low energies (below E_{th}) [8]. Based on the Arrhenius-like approach, the efficiency as a function of conversion can be displayed as in **Figure 3**.

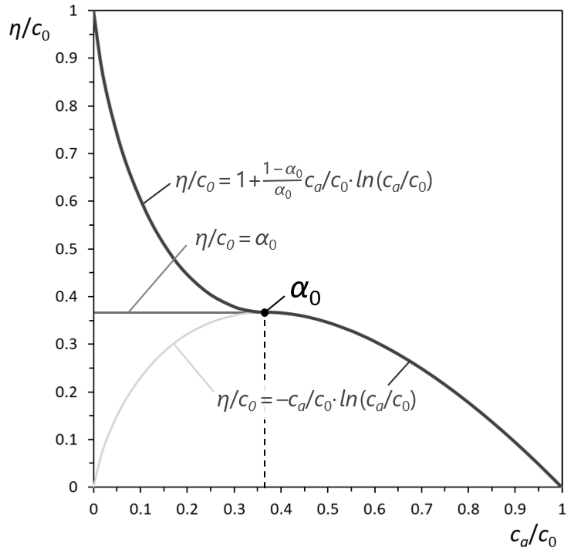

Fig. 3. Energy efficiency as a function of conversion (normalized to c_0). Arrhenius-like behaviour without enhanced conversion for SEI below the alpha point yield a $-x \cdot ln\, x$ function, while electron impact activated intermediates raise the energy efficiency up to α_0. Further enhanced efficiencies have been reported for CO_2 conversion due to ladder climbing that might be described by the dark grey slide-shaped function.

To meet constraints as given by the available energy per molecule and its energy distribution as well as being continuous in $E_{pl} = E_{th}$ (alpha point), here, a $+x \cdot ln\, x$ function is assumed to describe the additional energy transfer at $E_{pl} \leq E_{th}$. The observed 'slide-shaped' curve can now be compared to results from the literature, where a comprehensive overview is, for example, given by Snoecks and Bogaerts [8]. Recent results for CO_2 conversion in MW plasma agree well, which needs to be further investigated.

5. Conclusion

The specific energy input represents an appropriate parameter to describe chemical reactions in low temperature plasmas, where the Boltzmann energy distribution yields Arrhenius-like behaviour for the conversion of molecules into a demanded product. As the product, both plasma polymer films as well as gas conversion can be considered. While numerous examples in the field of plasma polymerization exist, strongly supporting optimization and upscaling, a first approach is made to address the field of gas conversion. As a perspective, energy efficiencies can be discussed as a function of conversion indicating the optimum that can be achieved by electron impact activation in low temperature plasmas compared to additional ways of energy transfer, probably depending on certain constraints. Furthermore, effects by thermal energy needs to be considered.

6. References

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