Complexity visualization and numerical simulation of plasma-activated liquid chemistry

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Abstract: Low-temperature plasma-activated liquids are gaining increasing attention because they can produce abundant reactive species. The interaction between plasma-induced reactive species and liquid solutions containing various components is extremely complicated and is a subject to be challenged. In this work, complexity visualization of reaction system and one-dimensional numerical simulation of liquid chemistry are conducted to reveal how various plasma species permeate into the liquid and what reactions are triggered.

Keywords: Complexity visualization, numerical simulation, liquid-phase chemistry.

1. Introduction

Low-temperature plasmas have been widely studied in the fields of biomedicine or agriculture. In these applications, plasma-activated liquids are gaining increasing attention because they can produce abundant reactive species, whereas the aqueous chemistry is complex and its mechanism is not fully understood. We still have some challenges to reach comprehensive understanding of the nature of plasma-induced liquid chemistry. This study proposes mathematical/numerical approaches to tackle the issue. The complex network analysis based on the graph-theory, one of the information mathematics, enable us to reveal the hidden feature of chemistry through the visualization and centrality-based identification of the reacting network structure [1-4]. Numerical simulation clarifies the influence of plasma irradiation on the liquid chemistry. A one-dimensional reaction-diffusion model with hundreds of reaction processes can quantify how various plasma species permeate into the liquid and what reactions are triggered.

2. Method

In graph theory, the elements and the interactions between these elements of the system are represented as nodes and edges, respectively. When we apply the graph theory to the plasma chemistry, the nodes correspond to species and the edges represent the connections among species in the reaction kinetics [1-3]. As an example, Fig. 1(a) and (b) show the schematic diagram of the outgoing- and incoming edges and nodes of the reaction $He+O_3 \rightarrow He+O(^3P)+O_2$, and the corresponding directed graph with out-/in-degree counts, respectively. Degree indicates the total number of edges that connect the node of interest with other nodes. Fig. 1(c) shows a diagram of topological measures closeness centrality and betweenness centrality. Closeness centrality is a measure of how quickly information spreads from one particular species in the network to other reachable species, and so those species with high closeness centrality are placed in the center of the network. The complex network analysis based on the graph-theory enables us to reveal the hidden feature of reacting chemistry through the visualization and centrality-based identification of the network structure.

The time-dependent one-dimensional (up to 10 mm depth from liquid surface) simulation based on reaction-diffusion model has been developed, where the chemical kinetics system includes 100 species and 500 reaction processes to explain the interactions between hydrogen, oxygen, nitrogen and chlorine with carbonic acid equilibrium. The concentration of species at the liquid surface, i.e., the inlet boundary condition, is estimated from the gas-phase concentration via Henry's law assumption. The numerical model clarifies the effect of inflow of various plasma-induced reactive oxygen / nitrogen species on the chemistry of air-saturated water or saline solution.

3. Results

Fig. 2 shows a network diagram of degree centrality in the chemical model for air-saturated water containing atmospheric nitrogen, oxygen and carbon dioxide. In this case, the liquid-chemical reaction set consists of the 75-species and 340-processes. Fig. 2 clearly visualizes that the species with the highest degree, OH, NO, O_2, H^+, OH^-, O_2^- and H_2O, are located at the most centre of the network diagram. The species with the second highest degree are for example HO_2, NO_3^-, CO_3^-, NO_2^-, H and H_2O_2. Those hub species, i.e., a few species are highly connected to others, act as the reaction driver and dominate the network topology as primary components.

Fig. 3 shows the result of numerical simulation, where x-axis; length from surface (depth), y-axis; time up to 1000 s, z-axis; species concentration. Fig. 3(a) shows the behaviour of the hydroxyl radical (OH) concentration. The OH is given as an impact from plasma, which starts from t = 10 s and ends at 110s. As suggested by the network analysis, the OH radical is one of the most important intermediate species that directly or indirectly bridges reactants and products. As well-known, the highly reactive, short-lived, OH radical steeply disappears in liquid (up to 1 micro meter depth). The loss of OH radical efficiently activates the liquid chemistry, in turn results in the production of hydrogen peroxide (H_2O_2) as shown in Fig. 3(b). The long-lived H_2O_2 penetrated into the bulk region slowly.

4. Conclusion

Complexity visualization through graph theory and complex network theory provided valuable insights into complex reaction data. Detailed numerical simulation quantified the rich chemistry induced by the influx of plasma-induced reactive species in the realistic air-saturated condition. The present mathematical/numerical approach revealed how various plasma-induced species permeate into liquid and what reactions are triggered.

5. Acknowledgements

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6. References

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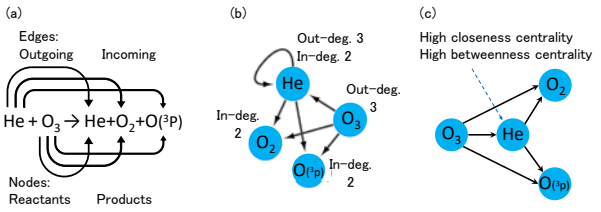

Fig. 1 (a) Schematic of outgoing- and incoming edges and nodes. (b) Directed edge diagram. (c) Centrality diagram.

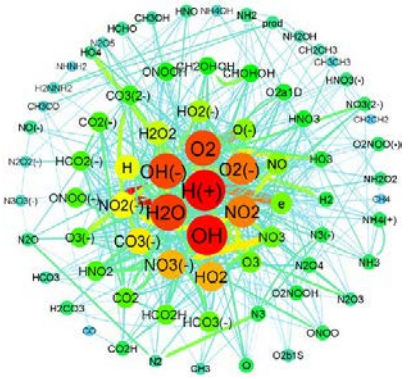

Fig. 2. Complexity visualization. Network diagram of the liquid chemical set. Species with high degree are illustrated as larger circle and located in the centre region.

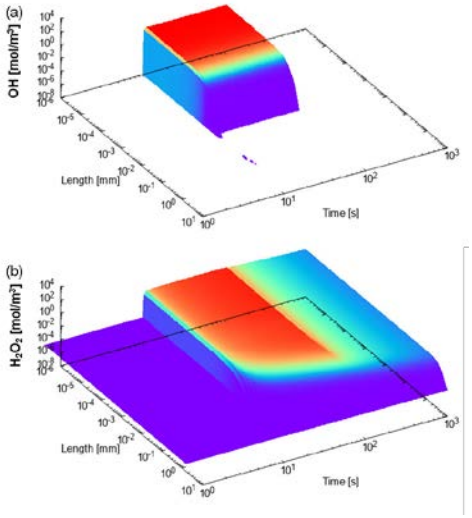

Fig. 3. Result of numerical simulation, Species concentration – Length from surface (depth) - Time. (a) OH radical impact from plasma. (b) H_2O_2 concentration.