UC Irvine Samueli
Department of Chemical and Biomolecular Engineering

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The Intriguing Role of Alkali Cations at the Electrified Interface in Electrocatalysis

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Abstract: Electrocatalysis at the electrode-electrolyte interface is fundamentally governed by electron transfer across the electric double layer (EDL), highlighting a crucial mechanistic link between electrocatalytic properties and EDL structure. A central question in this field is the role of alkali metal cations at this interface, commonly known as the "cation effect". This presentation will outline our ongoing research aimed at uncovering the fundamental principles underlying the cation effect in several important electrochemical reactions in aqueous environments.[1,2] Using advanced *in situ* analytical techniques,[3] we have discovered that alkali metal cations are not merely spectators, as traditionally believed, but actively influence the kinetics and mass transport in electrocatalysis. The identity and concentration of the alkali metal cation is critical in modulating electrocatalytic activity and selectivity,[4] as well as affecting electrode stability.[5] We will present a mechanism of cation-coupled electron transfer and its potentially interesting role in alkaline hydrogen evolution reactions. By gaining a deeper understanding of how alkali metal cations affect electrocatalysis, we will envision a novel conceptual framework for improving electrocatalytic processes.

References

1. Shin *et al.*, On the importance of the electric double layer structure in aqueous electrocatalysis, **Nat. Commun.** 13 (2022) 174.
2. Shin *et al.*, A unifying mechanism for cation effect modulating C1 and C2 productions from CO_2 electroreduction, **Nat. Commun.** 13 (2022) 5482.
3. Bae *et al.*, Unraveling the complex causality behind Fe-N-C degradation in fuel cells, **Nat. Catal.** 6 (2023) 1141.
4. Ji *et al.*, Alkali metal cations act as homogeneous cocatalysts for the oxygen reduction reaction in aqueous electrolytes, **Nat. Catal.** 7 (2024) 1330.
5. Kim *et al.*, Space charge, modulating the catalytic activity of single-atom metal catalysts, **J. Am. Chem. Soc.** 147 (2025) 4667.

Bio: Prof. Chang Hyuck Choi (CK) is an electrochemist and currently an Associate Professor in the Department of Chemistry at Pohang University of Science and Technology (POSTECH), Korea. He received his B.S. (2007) and Ph.D. (2012) degrees from the Department of Chemical Engineering at KAIST, Korea. After working as a postdoctoral researcher at KAIST, he was a Humboldt Research Fellow at the Max Planck Institute for Eisenforschung, Germany, from 2014 to 2016. From 2016 to 2022, he was an Assistant/Associate Professor in

the School of Materials Science and Engineering at GIST, Korea. He has authored more than 110 peer-reviewed journal papers. He is a member of the Young Korean Academy of Science and Technology (Y-KAST) and currently serves as an editor of the journal “Electrochimica Acta”.

Hosted by: *Prof. Iryna Zenyuk*