

Cation-Dependent Selectivity in Kolbe Electrolysis of Acetic Acid: Unlocking the Full Potential of the Reaction.

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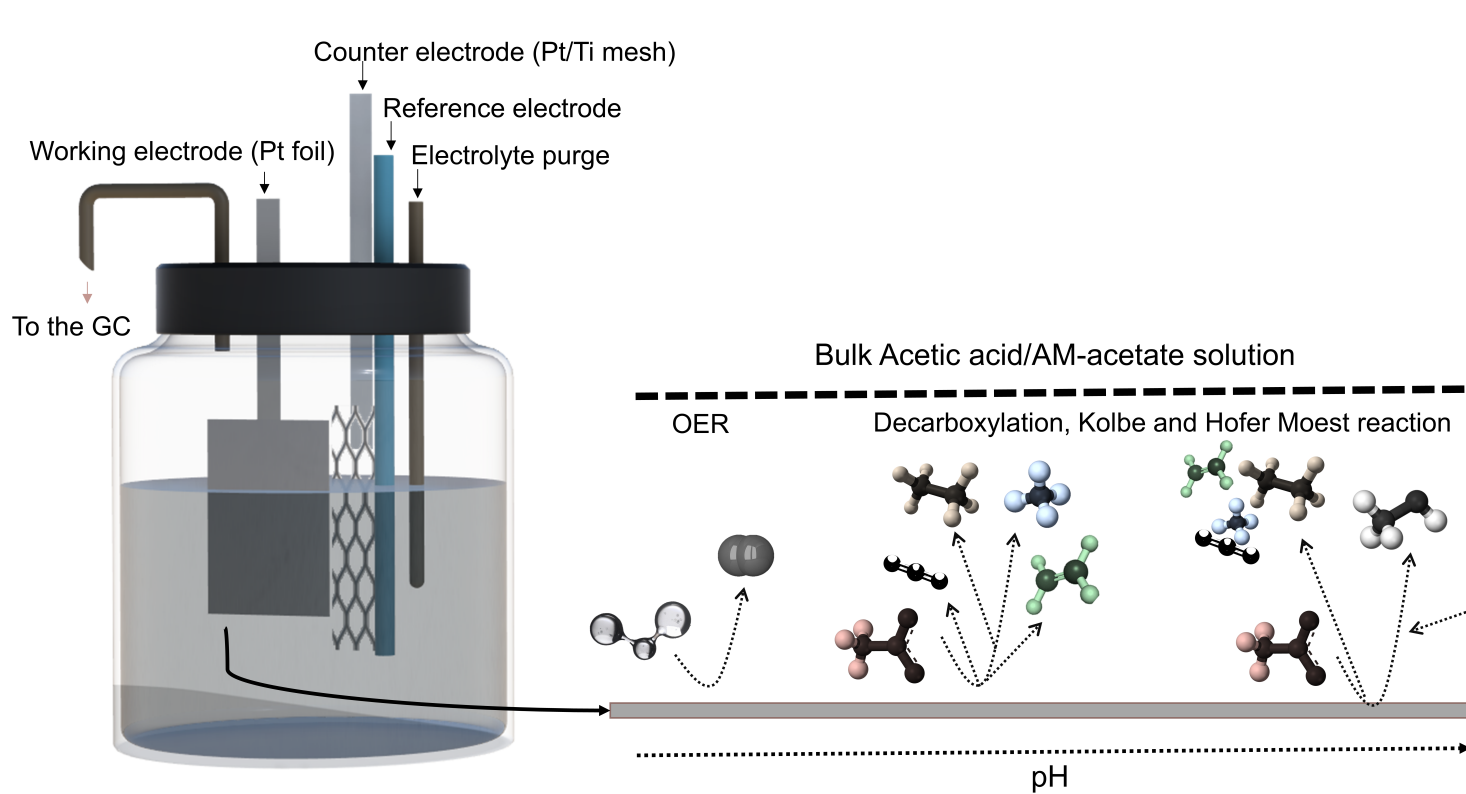
Summary

Question: Are alkali metal cations inert spectators during Kolbe electrolysis of acetic acid?

Task: Probing the reaction selectivity at different conditions via chronopotentiometry. Employing RRDE, cyclic voltammetry and EIS to deduce surface coverage and local pH.

Results: Product distribution and overall electrochemical activity are influenced by the presence of cations with K^+ being most suitable for Kolbe electrolysis (order of activity $Li^+ < Na^+ < Cs^+ < K^+$). The trend was observed irrespectively of the electrolyte throughout the entire pH range at low current densities (25 mA/cm^2), i.e. at pH 3 where OER is dominating, pH 5 where OER transitioned to Kolbe electrolysis and pH 9,12 where Hofer Moest reaction occurs.

Background



Carboxylic acids, a major fraction of pyrolysis oil can be transformed electrochemically in alkanes and alcohols by Kolbe and Hofer Moest reaction. The selectivity of electrochemical decarboxylation depends on various factors, i.e. electrode material and reaction conditions (supporting electrolyte, pH and current densities). Alkali metal cations (Li^+ , Na^+ , K^+ , Cs^+) are widely considered inert, a significant influence in electrochemical oxidation of methanol, ethanol, and formic acid is reported. It is assumed that oxygenated species present on the electrode surface form (strong/weak) non-covalent interaction with the alkali metal cations.

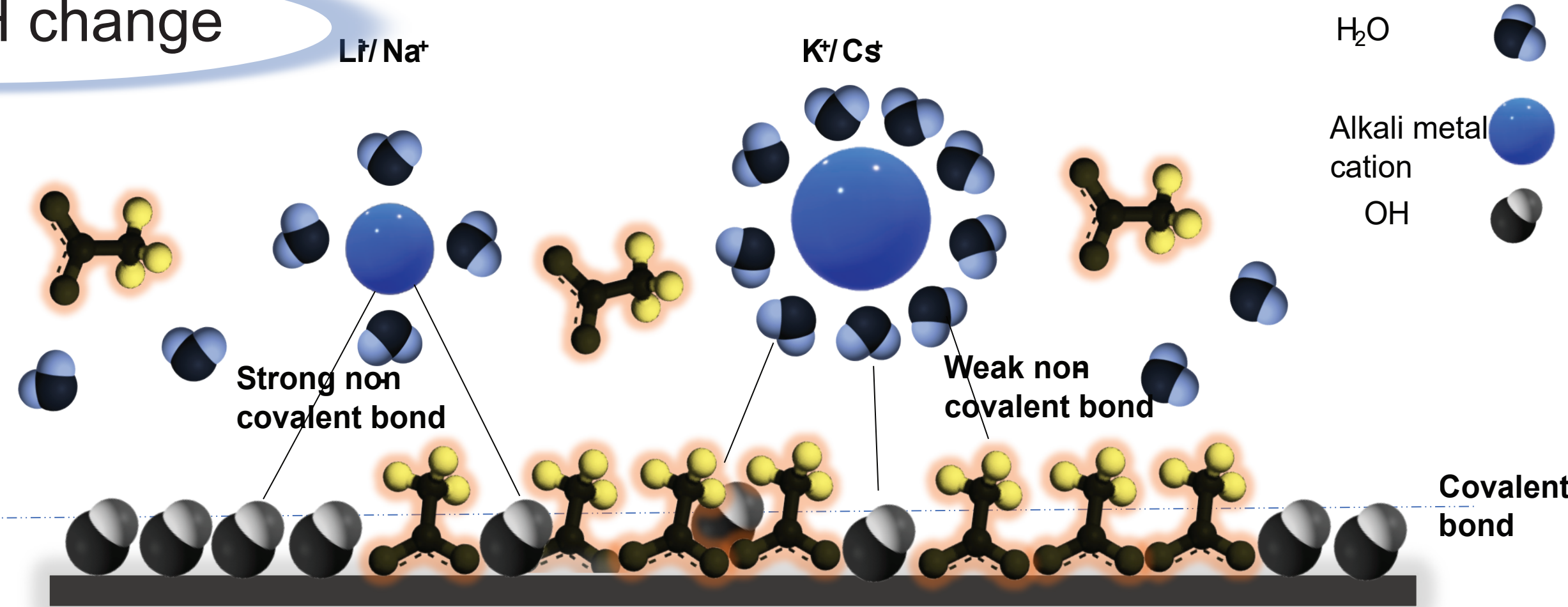
Results

Catalyst sites blocking effect

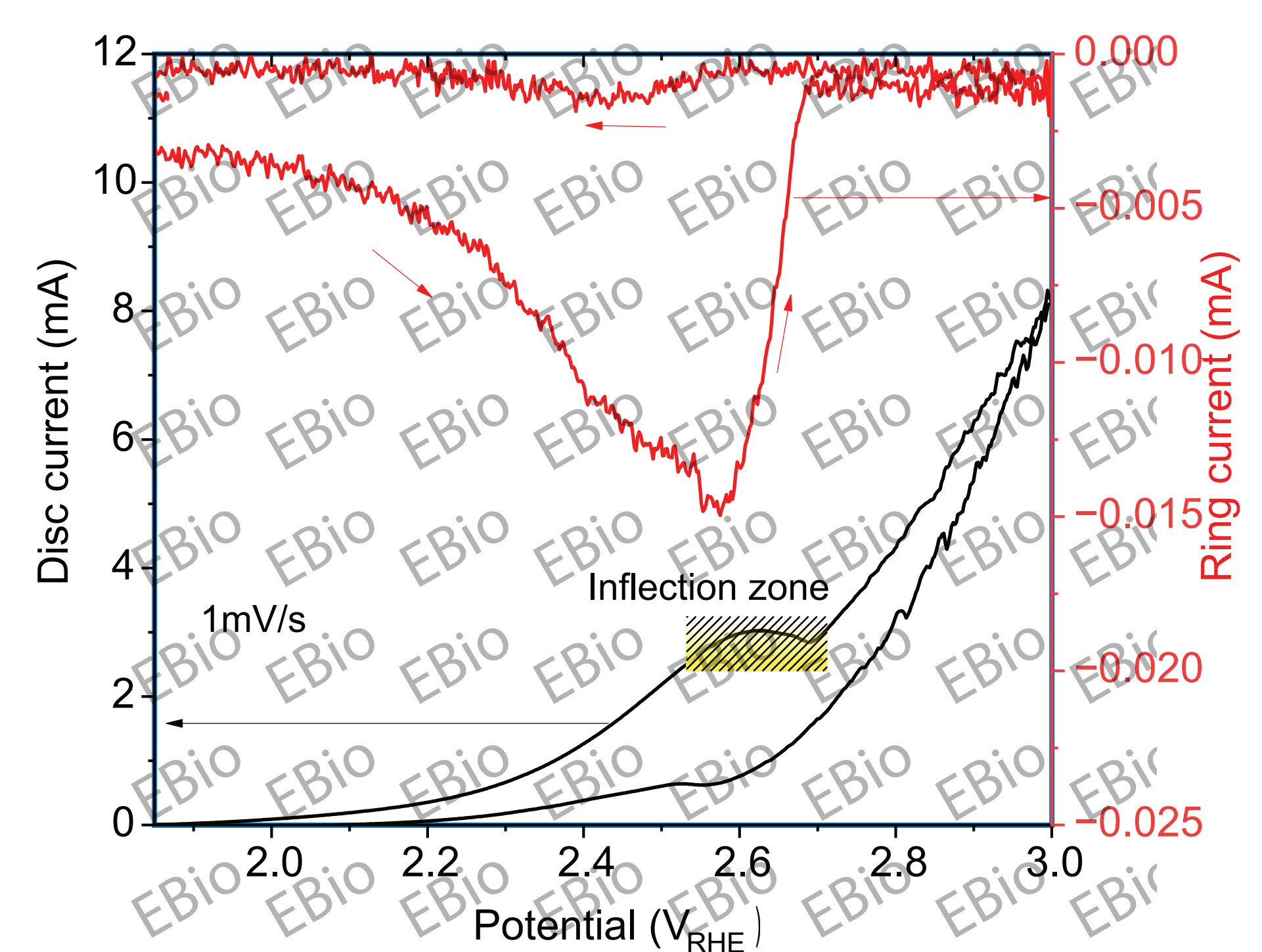
V drop: driving force effect

Chemical interactions: Cations vs intermediate

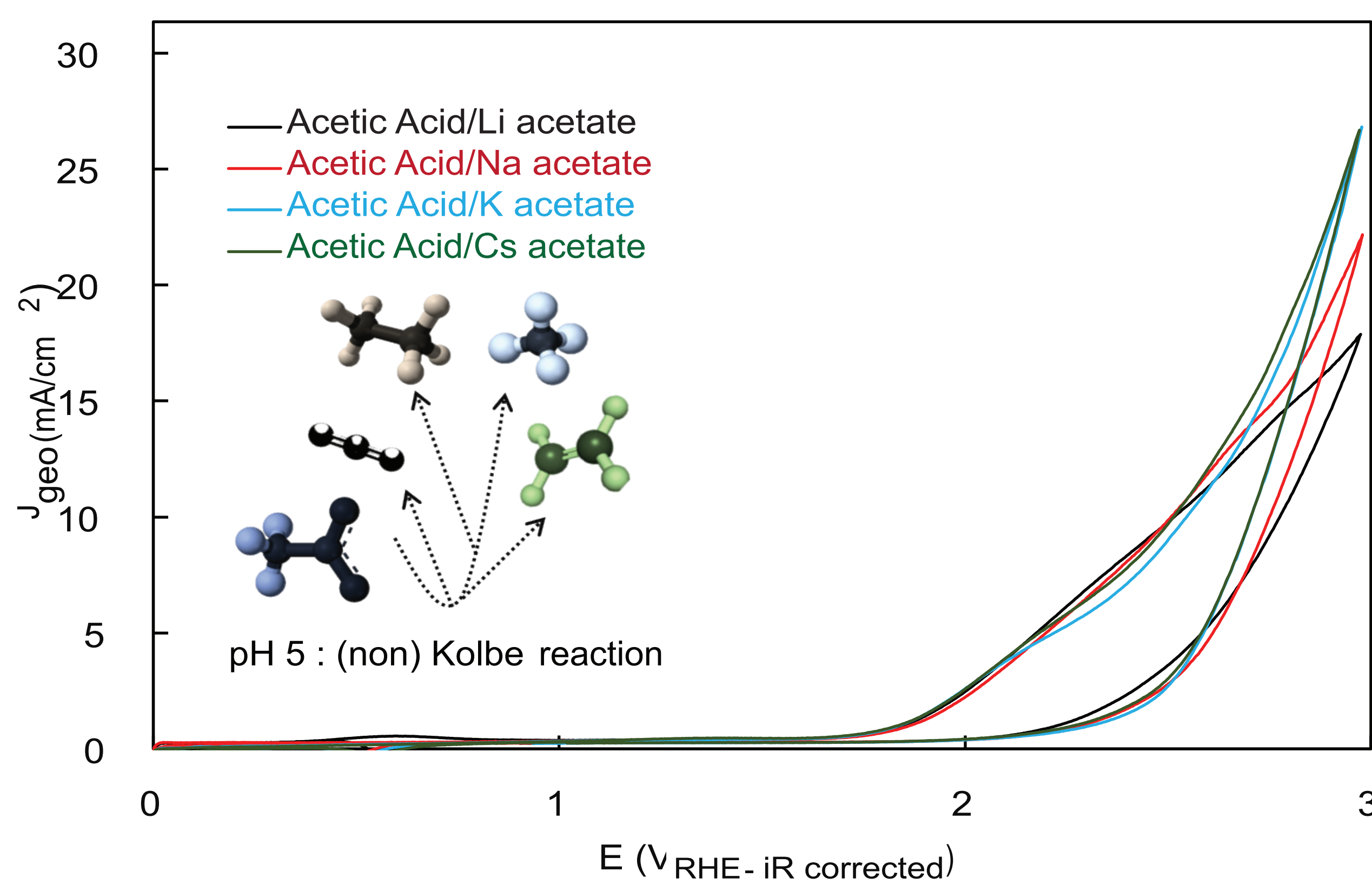
Interfacial pH change



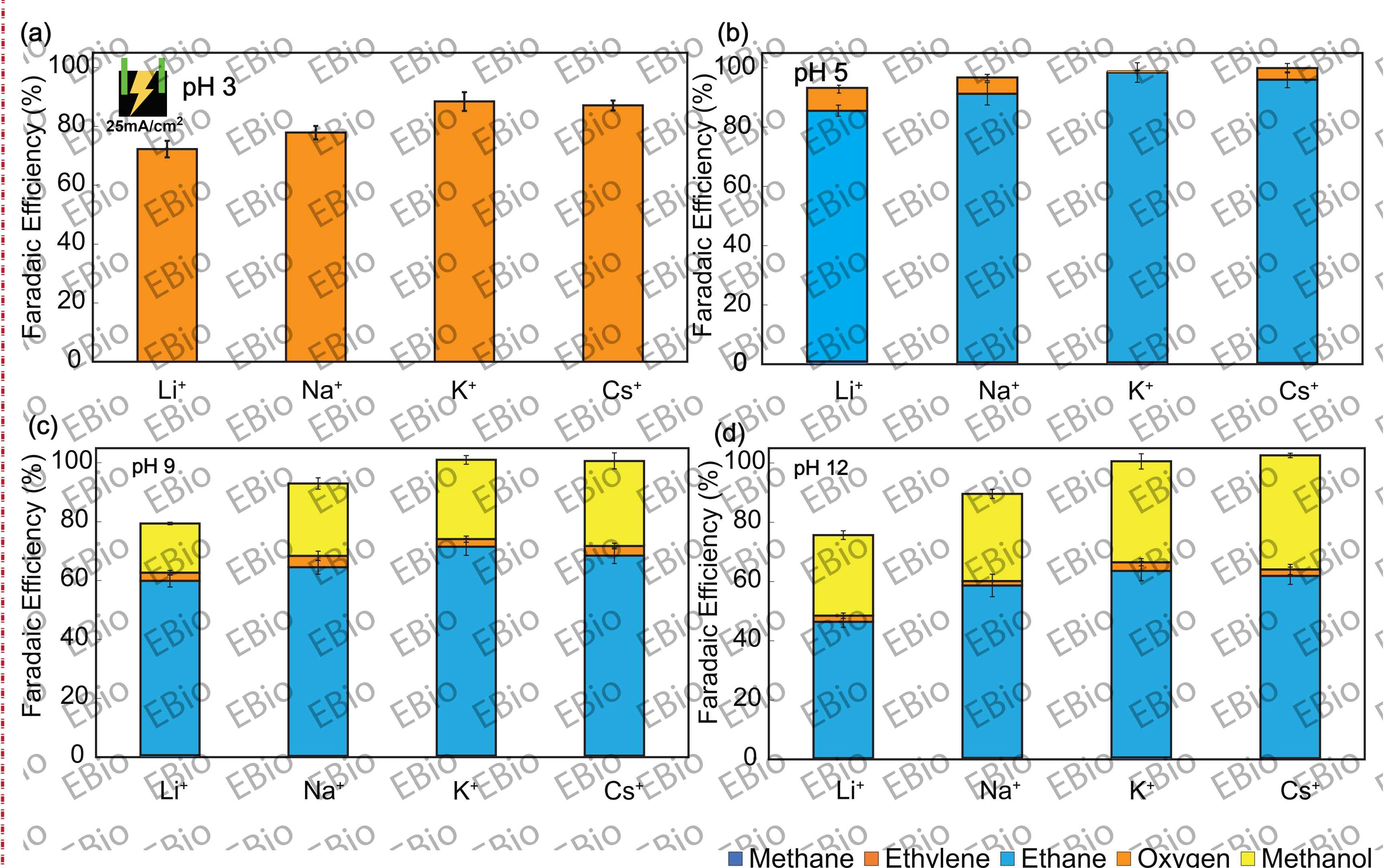
Schematic of the non-covalent interaction (strong Li^+/Na^+ , weak Cs^+/K^+) between alkali metal cations and surface oxygenates



"Inflection zone shows the transition of oxygen evolution reaction to Kolbe reaction"

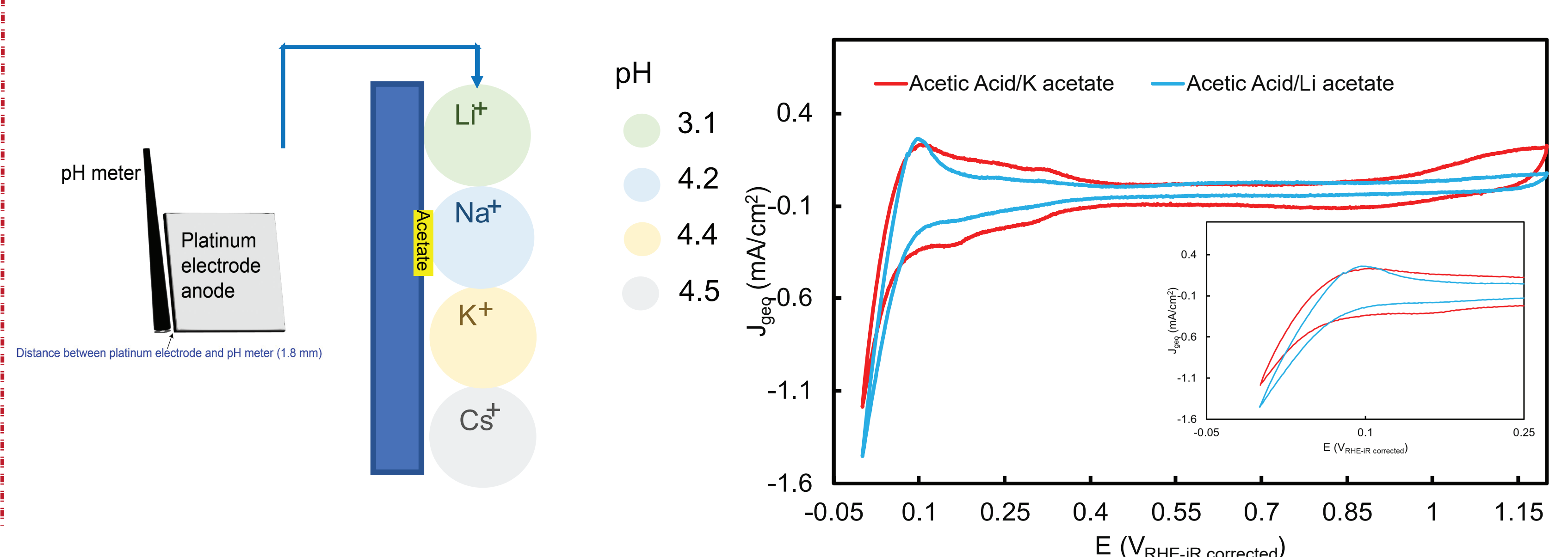
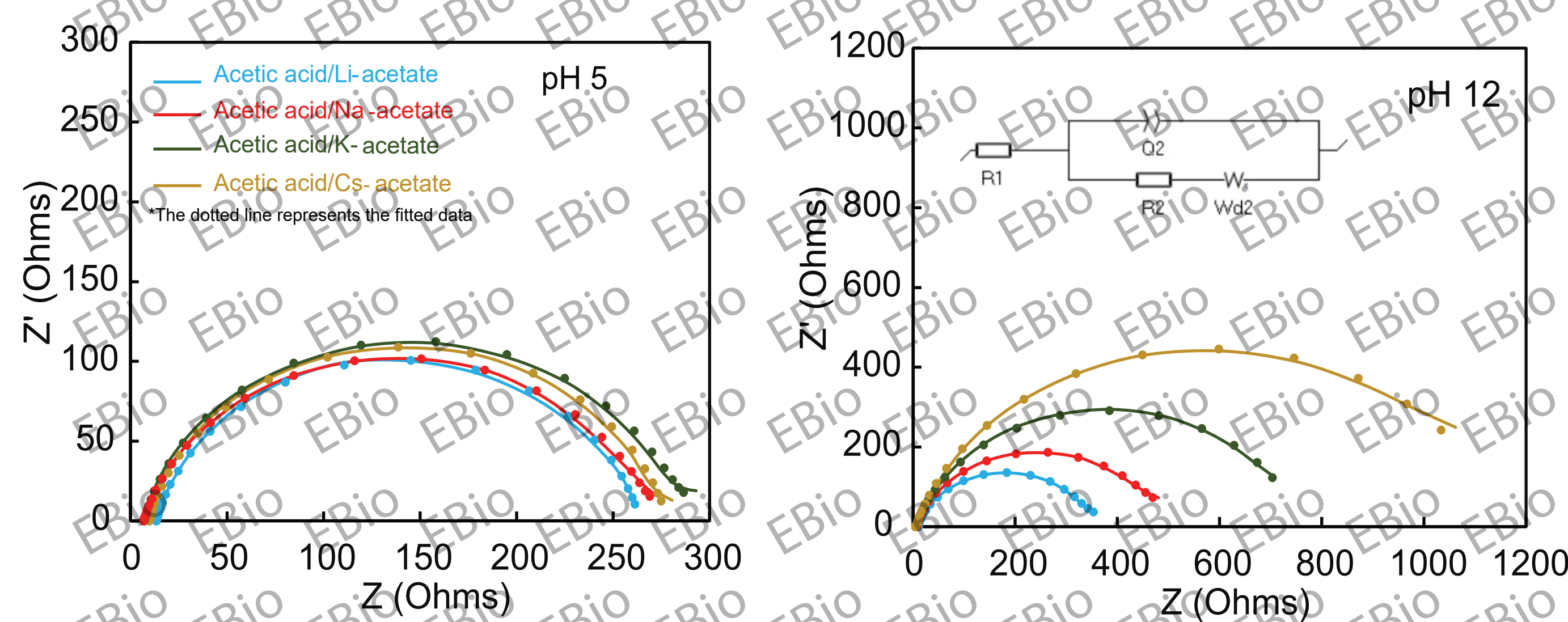


"Apparent differences in the CV profiles in the presence of different alkali metal cations show their influence during decarboxylation"



"The shift in selectivity of Kolbe reaction is presumably related to the changes in local pH"

"Differences in surface coverage in presence of alkali metal cations during Kolbe and Hofer Moest reaction is reflected by charge transfer resistance"



References

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