In Situ Studies of Molecular Electrocatalyst Speciation with the Electrochemical Quartz Crystal Microbalance

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Highlights

- EQCM can reveal deposition of heterogeneous material from molecular precursors.
- Corrosion processes complicate speciation studies and these can be studied by EQCM.
- Speciation routes can be assigned by combining EQCM data with chemical reactivity studies.
- EQCM can usefully measure catalyst homogeneity at short times during voltammetry.

1. Introduction

Stable catalysts are required for construction of systems capable of storing reducing equivalents as fuels like hydrogen (H_2). [1] Molecular fuel-forming catalysts attract significant attention because they are readily derivatized and can be studied in solution to gain mechanistic information. [2] Studies of mechanism in electrode-driven catalysis are challenging, however. The catalyst is in a dilute solution with a large excess of supporting electrolyte, and only a small amount of catalyst is electroactive in a given moment.

2. Methods

We show here that the electrochemical quartz crystal microbalance (EQCM) can be used to probe electrocatalyst speciation and/or decomposition in real time during electrode polarization. Chemical reactivity studies, informed by the EQCM studies, have been carried out to understand catalyst speciation upon introduction to the catalytic medium. Infrared and nuclear magnetic resonance spectroscopies have been applied to gain structural information.

3. Results and discussion

In this paper, we will discuss application of the EQCM to studies of molecular catalysis of proton reduction, and CO generation from CO_2. Mass changes at the electrode surface (measured by EQCM) due to deposition of heterogeneous material are readily measured down to nanogram levels. In the case of a fully homogeneous catalyst system, no mass change is registered. Heterogeneous materials formed in strongly acidic media can be transient in nature, and the EQCM reveals the formation and corrosion of these materials. Generally, we find that the precatalyst structure and the conditions chosen for catalyst operation strongly affect speciation behavior.

4. Conclusions

We have shown that the EQCM can be used to obtain information on speciation and/or decomposition of molecular electrocatalysts at short times during electrode polarization. [3] Taken together, our studies show that the EQCM is a useful tool for studies aimed at improving the stability of catalysts for fuel generation.

References

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Keywords
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