Enhancement of the Catalytic Activity of Nanoparticles by the Thermal Motion of a Polar Solvent

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The success of electrochemical devices for energy applications relies heavily on the development of efficient, stable, and cheap nanocatalysts, which has motivated intense research to elucidate what controls the catalytic activity at the atomistic level. Notably, the effect of size reduction on the intrinsic activity of nanoparticles is hard to predict in view of the complex and often conflicting behaviors of different contributions to the catalytic activity at the nanoscale. It is therefore important to be able to analyze the different factors and assess the magnitude of their contributions.

In this work, we discuss the enhancement of the catalytic activity of nanostructures under the effect of electrode potential fluctuations. Extending the insights of Krischer *et al.* [1], we propose that the potential of a nanoparticle in solution fluctuates in response to the thermal motion of the polar solvent, and these potential fluctuations may serve to enhance the catalytic activity with respect to a macroelectrode. We derive a simple estimate of the enhancement effect at a semi-phenomenological level by combining the empirical Tafel law and microscopic insights of the Marcus theory. For nanoparticles in the 3-5 nm range, we obtain an approximate 10-fold enhancement factor of the catalytic current compared to a macroelectrode.

This dynamical enhancement effect is characteristic of the nanoscale. It is thus particularly relevant in connexion with the intense development of spectroscopic and surface science probing techniques with high spatial, temporal, and spectral resolution, which will greatly advance the characterization of the dynamical behavior of nanostructures so as to optimize them for electrochemical applications.

[1] V. García-Morales and K. Krischer, J. Chem. Phys. 134, 244512 (2011).