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Electrocatalysis

Electrocatalyst nanoparticles go with the flow

Electric current is now shown to induce movement of the atoms in electrocatalyst nanoparticles, leading to morphological changes and performance degradation. This electromigration effect needs to be taken into account when designing nanostructured catalysts for electrochemical devices.

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Electrochemical generation of valuable chemical compounds — for example, by hydrogen evolution reactions (HER) or carbon dioxide reduction reactions (CO₂RR) in an electrolyser — is considered a promising way of storing the excess electrical energy that is produced by intermittent renewable sources of electricity, such as wind and solar power. In general, these electrochemical energy conversion technologies are reliable but suffer from high investment costs. To make them more appealing for large-scale use, the overall efficiency and lifetime must be improved. Hence, efficient electrochemical fuel generation requires more active and stable electrocatalysts. Typically, platinum-group metals show these properties and hence serve as catalysts on the electrodes^{1,2}. As these materials are scarce and expensive, it is important to maximize the available surface area using nanoparticles, to obtain the best mass activity. Unfortunately, the stability of the nanoparticles decreases with decreasing size³. In the long run, use of the electrolyser results in performance degradation, partly due to agglomeration of the nanoparticle catalysts and partly due to dissolution of the metal species.

Some of the mechanisms for nanoparticle instability are yet to be understood fully. For example, catalyst stability has been investigated by correlating dissolution rates with thermodynamic properties such as metal–metal and metal–oxygen bond strengths⁴; however, when the electrode potential is changed, for example during the start-up or shut-down of the electrolyser, the metal catalyst oxidation state can change, as dictated by its thermodynamic properties. Insight into the phase-changes and induced stability issues can be obtained by examining Pourbaix diagrams, which depict the thermodynamically stable phase (metallic, oxide, hydroxide and so on) as a function of applied potential and electrolyte pH. During these transitions between the metallic state and other phases, kinetic effects are expected to play a role in the metal stability⁵.

The above-mentioned processes frequently take place if the electrolyser is used to convert excess electrical energy into chemical bond energy in solar panel or windmill parks during the peak production periods. However, long steady operation periods are also expected to take place. There, the processes governing the catalyst stability can be expected to differ from the processes that occur during the transition periods. Therefore, to maximize the electrolyser

lifetime, understanding the phenomena affecting the stability of the catalysts both during the varying potential and stable operation conditions is of utmost importance.

Now, reporting in *Nature Catalysis*, Klinkova and co-workers⁶ have approached the problem of catalyst instability by preparing shape-controlled model nanoparticles and studying their degradation using identical location electron microscopy analyses of the particle morphology after the reaction. Results from the experimental work are combined with quantum chemical calculations of metal-reactant-stability and finite element models of the electric field effects and current-crowding.

Klinkova and her colleagues have prepared branched and core-cage nanoparticles from Au and Pd. Although these materials do not represent the best known catalysts for these reactions, they are chosen for their stability and activity in both HER and CO₂RR. As small nanoparticles tend to be less stable, one would intuitively think that fine features, such as the branches of the nanoparticles in this study, would be the most vulnerable and easy to degrade. However, electron microscopy images show that this is not the case. Instead, the catalysts degrade from the bottom, where the particles are in contact with the electrically conducting support (Fig. 1). This is explained by structural changes that result from two phenomena during the electrocatalytic conversion of the reacting species into the products. One of those is related to the progressing electrochemical reactions as the adsorbed reacting species and intermediates weaken the metal-metal bonds in the catalyst particles and consequently induce metal atom rearrangements. This kind of reaction-driven structural transformation can also occur during heterogenous catalysis. The second driving factor is specific to electrochemical reactions and related to current-distribution profiles in the metal nanoparticles catalysing the electrochemical reactions. Local differences in the current induce electromigration of the metal atoms to minimize current-crowding, as illustrated in Fig. 1. Therefore, the complex nanoscale morphology of the catalyst nanoparticles affects metal atom redistribution during the electrocatalytic reactions. Electromigration is a well-known effect in semiconductor research⁷, but now it is shown to have a considerable effect on the stability of the catalyst particles.

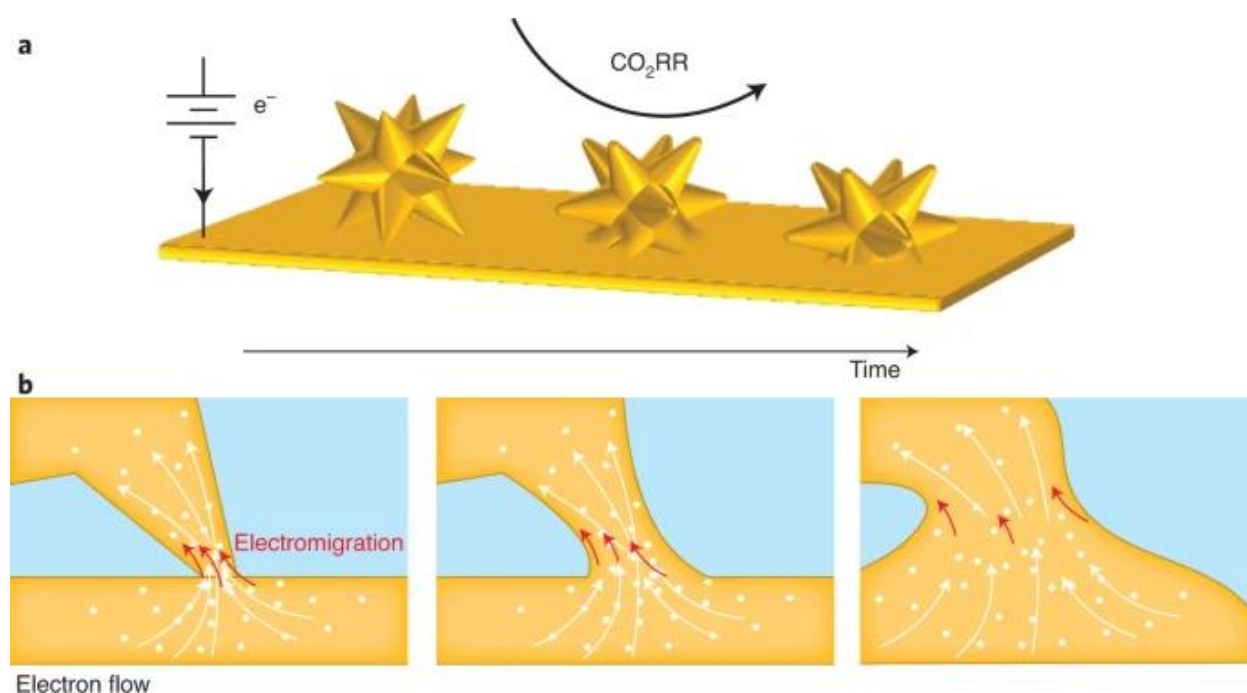


Fig. 1: Schematic representation of the concepts described in the work by Klinkova and colleagues. a, Electromigration induced reshaping of the catalyst particles during operation. b,

Illustration of the electromigration process decreasing the current crowding. Panel a adapted with permission from ref. 6, Springer Nature Ltd.

While evaluating the movement of surface atoms will require quantum chemical calculations, current-distribution can be analysed with a normal desktop computer. This work will help to design more stable catalyst nanostructures, as structural stability of the catalyst can be predicted beforehand and structures minimizing electromigration-induced degradation can be designed.

The performed measurements are very complicated and they introduce a way to study and better understand the degradation of the catalyst nanoparticles by electromigration. There are still some open questions, including the effect of changing pH, as CO₂-saturated solutions have a significantly different pH than solutions without CO₂. Pd is an interesting choice of material for HER. Unlike most other electrocatalysts for this reaction, Pd is able to absorb up to 1:1 ratio of atomic hydrogen into the lattice, forming Pd-H, giving an additional source of H available to generate hydrogen⁸. The effect of the hydride formation has not been discussed in the paper. Additionally, it is unclear if the decrease in catalytic performance is only due to the changing nanoparticle morphology, or if contaminants — for example, some of the CO₂RR products — could contribute to poisoning of the catalyst surface.

Nevertheless, this work is important in the investigation of catalyst stability. It would be interesting to see this approach applied to more relevant catalysts, such as Pt or Ni for HER, and Cu for CO₂RR

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