2000

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We describe an application of the scanning electrochemical microscope that utilizes tip-sample feedback to characterize the reactivity of electro-oxidation catalysts. The kinetics of hydrogen oxidation are probed at a platinum electrode as a function of applied potential in aqueous sulfuric acid solution. Tip-sample feedback generates a tip response that reflects the rate of hydrogen oxidation at the substrate. The ability to directly measure the rate constant for hydrogen oxidation is, subsequently, used to perform reactivity mapping of heterogeneous electrodes consisting of catalytic and noncatalytic domains. Differences in reaction kinetics clearly distinguish surface composition variations based upon their reactivity toward hydrogen oxidation and illustrate the capability of this technique as a screening tool in the design of electrocatalysis. Further experiments investigating the oxidation of methanol illustrate the ability to characterize complex multistep reactions.

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Manuscript submitted February 16, 2000; revised manuscript received April 26, 2000.

A renewed interest in fuel cells has emerged in an effort to develop commercially viable high energy density power sources that are portable and environmentally friendly.¹⁻⁸ The properties of the fuel cell's anode catalyst have received considerable attention. These efforts have focused on the development of an improved understanding of the reaction pathways associated with the oxidation of hydrocarbon fuels such as methanol and formic acid,⁹⁻¹² fabrication of poison-resistant and highly active anode materials,¹³⁻¹⁷ examination of the interplay between catalytic activity and poison susceptibility at single crystal and polycrystalline electrodes,^{18,19} and development of combinatorial synthesis methods and efficient screening tools for the discovery of highly active multicomponent catalyst materials.^{20,21} Recent advances include the discovery of an "optimized" multicomponent catalyst for methanol oxidation,^{20,21} construction of high surface area and poison-resistant nanoscale anodes,^{22,23} and development of a detailed understanding of the role of crystal orientation and composition on reactivity and poisoning of numerous binary catalyst compositions.^{13,24-26}

The hydrogen oxidation reaction (HOR) represents the primary anode reaction for low temperature fuel cells that operate using pure hydrogen gas or hydrogen derived from synthesis gas. HOR has been extensively studied on pure and multicomponent metal catalysts in order to develop an understanding of the reactivity of various catalyst surfaces, the influence of surface structure and crystal orientation on reactivity, and the role of various electrode-deactivating poisons and reaction intermediates, which include carbon monoxide and a variety of strongly adsorbing anions, as well as the impact of activity-enhancing species, such as underpotentially deposited metals.²

A great deal of fundamental kinetic information about HOR has been gleaned through the use of hydrodynamic methods such as the rotating disk electrode (RDE).^{14,16-18,26-28} However, mechanical limitations and the onset of fluid turbulence limit the ability of RDE techniques to access extremely high rate constants. However, the high mass transfer rates achievable at microelectrodes have allowed access to kinetic regimes in excess of those typically obtainable with RDE techniques. In fact, the combination of a microelectrode and capillary jet has been shown to produce mass transfer characteristics equivalent to a RDE rotating at 200,000 Hz.²⁹ Alternatively, the ability of a scanning electrochemical microscope (SECM) to position a microelectrode probe near a substrate-electrolyte interface creates mass transfer between tip and sample (proportional to their separation) that is sufficiently high to allow access to kinetic rate constants two to three orders of magnitude higher than that allowed with RDE.³⁰ In addition,

the ability to perform interfacial measurements as a function of spatial position allows the SECM to perform direct structure-function measurements on catalytic surfaces by imaging variations in reactivity with changes in surface composition or structure.

In this paper we describe an application of the electrochemical microscope that utilizes tip-sample feedback to characterize the kinetics of electro-oxidation reactions on a variety of electrode surfaces. We describe potential dependent measurements of the rate of the hydrogen oxidation reaction on a polycrystalline platinum substrate electrode. This technique is further used to image reactivity as a function of spatial position in order to characterize the catalytic activity of several patterned substrate electrodes comprising reactive platinum and nonreactive silica or gold domains. Potential and position dependent reactivity mapping is used to demonstrate the interplay between surface composition, substrate potential, and catalytic activity. Extensions of this technique to the oxidation of methanol are also demonstrated.

Experimental

Materials.—Electrolyte solutions containing sulfuric acid H₂SO₄, sodium sulfate Na₂SO₄, and methanol CH₃OH were used as received (Aldrich, Milwaukee, WI). All experiments were performed using electrolyte dissolved in 18 MΩ deionized water (Milli-Q, Millipore Corp., Bedford, WA) and de-aerated with argon (BOC Gases) prior to measurement.

SECM.—The scanning electrochemical microscope (SECM) used in this work was similar to that described in the literature.³¹⁻³⁴ Three inchworm translation motors (model IW-710, Burleigh Instruments, Inc., Fishers, NY) were mounted directly onto one TS-300 (z) and two TS-100 (xy) translation stages configured for three-dimensional orthogonal motion. These stages were mounted directly to a vibration isolation platform and the entire assembly was enclosed in a Faraday cage. The inchworm motors had a 25 mm range of motion with mechanical resolution of 4 nm and optical encoders giving an absolute position reproducibility of 0.5 μm. Position control was achieved with a Series 7000 controller (Burleigh Instruments, Inc., Fishers, NY) interfaced to a GPIB-PCIIA IEEE-488 interface card (National Instruments, Austin, TX). Electrochemical measurements were performed using a bipotentiostat (model AFDRE, PINE Instrument Company, Grove City, PA) coupled with a high sensitivity current amplifier (Keithley Instruments, Inc., Cleveland, OH), which was used to measure the current at the microelectrode tip. Data collection and tip scanning were achieved with a multichannel data acquisition board (PCL818, Advantek, Minnetonka, MN) and a custom designed software program written in Visual Basic.

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Electrodes.—The microelectrode tips employed in the SECM were fabricated with 25 μm diam platinum or gold wires (Goodfellow, Berwyn, PA) using a technique similar to that described in the literature.³⁵ The tip of a borosilicate capillary tube (2.0 mm outer dimension, 0.5 mm inner dimension) was melted in a methane-oxygen flame until the tip sealed. A 25 μm diam platinum electrode wire was inserted into the capillary tube and sealed in the glass by pulling a vacuum on the open end while simultaneously heating the sealed end of the glass with a coil of nichrome wire. Once several millimeters of the glass sealed around the wire, heating was interrupted and electrical contact was made to the platinum wire with a copper wire through the open end of the tube using either mercury or a silver epoxy (Epotek, Billerica, MA) and cured. The connecting wire was then fixed into place with Conap Easypoxy (Conap, Inc., Olean, NY) and cured at 100°C for a period of 4 h. Once sealed, the tip was polished using an automated polishing wheel (Beuler, Lake Bluff, IL) with successively finer grades of emery paper (600 and 1200 grit) followed by diamond polishing paste (9 and 3 μm) to achieve a conical shape with a disk-in-plane geometry for the tip and a glass to metal ratio (R_g) of >10:1. Following initial shaping, tip electrodes were polished to mirror smoothness using 1 and 0.05 μm silica polish, sonicated in an ethanol/water solution, and rinsed with copious amounts of deionized water before use.

Substrate electrodes consisted of 2 mm diam commercial polycrystalline platinum disk electrodes (Bioanalytical Systems, West Lafayette, IN) incased in PEEK or homemade platinum electrodes sealed in glass. Electrode pretreatment consisted of polishing with successively finer grades of emery paper followed by diamond polishing paste until the electrodes exhibited a mirror finish. Platinum-gold array electrodes were created by electroplating platinum from a solution of 10 mM H_2PtCl_6 in 1 M H_2SO_4 through a patterned photoresist. The photoresist was then removed to expose gold and platinum regions. Before use, the substrate electrodes were sonicated in a methanol/water solution and then rinsed with copious amounts of deionized water. Electrode pretreatment was achieved by potential cycling between water oxidation and hydrogen evolution in 0.5 M H_2SO_4 solutions.

Results and Discussion

The cathodic response of a 25 μm diam gold microelectrode in an electrolyte solution of 0.01 M H_2SO_4 in argon saturated 0.1 M Na_2SO_4 is shown in Fig. 1a. On this scale, the electrode exhibits minimal current at potentials positive of -0.5 V but an appreciable cathodic current corresponding to the reduction of protons (H^+) to dihydrogen (H_2) at more negative potentials

Although the formal potential of the hydrogen (H^+/H_2) couple resides at roughly -0.25 V on this potential scale, gold exhibits a large overpotential for the hydrogen evolution reaction (HER).³⁶ Therefore, appreciable reduction of hydrogen (H^+) is not observed until potentials negative of -0.5 V are reached. A steady, mass transfer-limited reduction current is achieved at potentials between -0.9 and -1.4 V. Bulk water reduction occurs at potentials negative of -1.4 V. A steady plateau current in the diffusion-limited region is maintained for this reaction under conditions where tip contamination can be avoided and bubble formation does not occur. The latter is associated with the solubility limit of H_2 in this solution and typically requires hydrogen concentrations of less than 0.05 M. Further negative excursions in the tip potential (less than -1.4 V) results in the reduction of bulk water and vigorous H_2 bubbling at the probe tip. The diffusion-limited current for hydrogen reduction under these conditions is -340 nA.

With the microelectrode tip held at a potential of -1.2 V (denoted with * in Fig. 1a), the reduction of protons to hydrogen occurs at a diffusion-limited rate. Under these conditions, the SECM probe can perform a variety of functions when placed near a substrate interface (Fig. 1b), which include the dosing of H_2 to the substrate interface, detection of H^+ produced or in the tip-substrate gap, and

increasing the local solution pH. In the feedback mode, H_2 that is generated at the tip diffuses to the substrate and is oxidized to form H^+ , which can diffuse back to the tip and contribute to additional tip current. In this mode, the tip current will reflect the rate of the hydrogen oxidation reaction at the substrate and can be used to extract the value of the substrate rate constant.

The tip-substrate interface in the SECM system has been successfully modeled by considering the concentration of probe species, or in this case the hydrogen generated and the protons consumed at the tip electrode, by solution of the diffusion-reaction problem in cylindrical coordinates. For hydrogen this problem is given by^{30,37}

$$\frac{\partial C_{\text{H}_2}}{\partial t} = D_{\text{H}_2} \left(\frac{\partial^2 C_{\text{H}_2}}{\partial z^2} + \frac{1}{r} \frac{\partial C_{\text{H}_2}}{\partial r} + \frac{\partial^2 C_{\text{H}_2}}{\partial r^2} \right) \quad [2]$$

and for protons is given by

$$\frac{\partial C_{\text{H}^+}}{\partial t} = D_{\text{H}^+} \left(\frac{\partial^2 C_{\text{H}^+}}{\partial z^2} + \frac{1}{r} \frac{\partial C_{\text{H}^+}}{\partial r} + \frac{\partial^2 C_{\text{H}^+}}{\partial r^2} \right) \quad [3]$$

Since the tip is held at a potential where the reaction is diffusion limited, the concentration of H^+ at the tip-electrolyte interface is zero

Figure 1. (a) Cyclic voltammetry of 25 μm diam Au microelectrode in argon-purged 0.01 M H_2SO_4 and 0.1 M Na_2SO_4 at a scan rate of 20 mV/s. (b) Schematic of tip-sample interface at large (left) and small (right) separations.

and the H_2 concentration is determined by the rate of H^+ reduction. The boundary condition at the substrate electrode is determined by the rate of hydrogen oxidation. If we consider a first order rate expression for the hydrogen oxidation reaction, the substrate current is given by

$$\frac{i}{nFA} = D \frac{dC_{H_2}}{dz} = k_{b,s} C_{H_2} \quad [4]$$

where $k_{b,s}$ is the rate constant for hydrogen oxidation in units of $cm\ s^{-1}$. The back reaction of H^+ to H_2 is assumed to be negligible at the substrate. A solution to Eq. 2 and Eq. 3 under steady-state conditions as a function of tip-substrate separation provides a series of working curves for the tip's current response.^{37,38} These working curves can be fit to the tip current, which is frequently normalized with respect to the current at infinite tip-substrate separation ($i_{T\infty}$). Since the tip-substrate separation and tip radius are known, the only adjustable parameter in this model is the electrochemical rate constant $k_{b,s}$. This fitting procedure has been successfully applied in the measurement of rate constants for systems ranging from liquid-liquid interfaces to a variety of heterogeneous electrochemical reactions.^{30,37} We have applied this methodology to characterize the hydrogen oxidation reaction on platinum electrodes as a function of applied potential,^{39,40,a} in the presence of surface adsorbates that produce oscillatory dynamics,⁴¹ and in the presence of electrode deactivating species such as carbon monoxide.⁴¹

Variations in substrate reactivity can also be resolved by performing tip-substrate voltammetry, where the tip is held at a fixed position and the substrate potential is scanned. Figure 2a depicts the tip current, which is normalized to the value at infinite separation, as a function of substrate potential for tip-sample separations between 100 and 2 μm . Figure 2b shows the substrate current under the same conditions. At 100 μm separation, the tip response is uniform, with a nearly constant current level at the bulk diffusion-limited value ($i/i_\infty = 1$). At this separation, the substrate response is that of the platinum surface, which unaffected by the tip (Fig. 2b, dashed line). Decreasing the separation to approximately 2 μm gives a potential dependent current response at the tip and an enhanced anodic current in the substrate scan. The tip current varies from a large value, reflecting positive feedback, at low substrate potentials to a small value, reflecting negative feedback, at positive substrate potentials. The positive feedback correlates with an increase in the anodic current at the substrate during both forward and reverse scans due to dosing of H_2 to the substrate interface, which is oxidized back to H^+ at potentials where the substrate is active. The change in tip response and the enhanced anodic current at the substrate directly tracks results seen in approach curve measurements.^{39,40} Positive tip feedback and excess anodic substrate current reflect a high rate constant for hydrogen oxidation while negative feedback and the lack of excess substrate current reflect a low rate constant. The abrupt drop in tip current on the positive sweep starting at 0.6 V corresponds to the formation of platinum oxide, while the increase in current on the negative sweep at 0.5 V reflects removal of the oxide layer. The tip current reaches a maximum plateau between -0.3 and 0.4 V. This plateau is due to diffusion-limited transport between the tip and substrate. An additional variation in tip current is observed between -0.3 and 0 V, which is the result of hydrogen adsorption and desorption on the substrate surface. Thus, the tip responds to variations in both the substrate rate constant and also to transient adsorption/desorption events when the substrate potential is scanned. These effects can be decoupled by using a combination of steady-state and transient experiments.

The ability to measure potential dependent catalytic activity suggests the possibility of using this as a general technique for characterizing spatially localized surface reactivity. For example, the kinetics of the hydrogen oxidation reaction can be measured locally to

evaluate the position dependent reactivity of a substrate toward this reaction. Catalytic activity is observed as a variation in tip current due to a changing substrate rate constant. As a demonstration of this concept, we have devised a variety of substrates with localized variations in surface composition. For example, Fig. 3 depicts the behavior of a substrate comprised of a 25 μm diam platinum microelectrode disk embedded in an insulating and nonreactive glass plane. These SECM images, which are plotted on a normalized current scale (the scale has been inverted for improved contrast), depict the current response over a platinum disk at substrate potentials of 0.0 (Fig. 3a) and 1.1 V (Fig. 3b) at a fixed tip-substrate separation of 10 μm . With the substrate potential held at 0.0 V, the tip current is low over the nonreactive glass regions while it is high over the platinum disk. According to kinetic measurements, the platinum substrate exhibits a hydrogen oxidation rate constant greater than 10 cm/s when held at a potential of 0.0 V.³⁹ Thus, the greater current over the platinum region is due to positive feedback. Although there is evidence of a slight sample tilt, with the lower left corner of the image ($X = 0\ \mu m$, $Y = 0\ \mu m$) being closer to the tip than the right

Figure 2. (a) Normalized tip current in argon-purged 0.01 M H_2SO_4 /0.1 M Na_2SO_4 at tip-substrate separations of 100, 50, 20, 10 (dashed lines), and 2 μm (solid line), acquired while the substrate potential is scanned between -0.3 and 1.3 V at 200 mV/s with the tip potential held at -1.2 V. (b) Cyclic voltammetry at platinum substrate in the presence of a microelectrode generating H_2 via H^+ reduction at 100 μm (dashed line) and 2 μm (solid line) tip-sample separations.

^a We have recently learned of similar experiments being performed by Allen Bard and co-workers in the Department of Chemistry and Biochemistry at the University of Texas at Austin.

($X = 200\ \mu\text{m}$, $Y = 200\ \mu\text{m}$), the remaining tip response can be attributed solely to the differences in reactivity between platinum and glass regions and the size of the reactive platinum disk, which in this case is comparable in size to the SECM tip.

The SECM image of the substrate electrode when it is held at a potential of 1.1 V (Fig. 3b) gives a considerably different picture. At this potential, the platinum electrode is coated with an oxide layer. According to kinetic measurements, the rate constant for hydrogen oxidation has dropped by several orders of magnitude in the oxide region as compared to the platinum metal. This converts the platinum electrode into a nonreactive surface. As a consequence, the tip response of Fig. 3b exhibits nearly pure negative feedback and the platinum region appears indistinguishable from the insulating glass region. This result clearly demonstrates the ability to detect variations in surface reactivity that result from composition variations on a surface. The activity of the platinum surface is seen to turn on at low potentials where the highly active metal surface is exposed (Fig. 3a), while the activity turns off at potentials where the surface is covered with the less active, metal oxide (Fig. 3b).

The ability to detect differences in reactivity on compositionally heterogeneous surfaces represents a unique method for performance-

based characterization and screening of catalytically active materials. In particular, images can be created that reflect catalyst performance as a function of position. On surfaces with a well-known surface composition, these images can be converted into measures of reactivity as a function of composition. As an example of this methodology, Fig. 4 depicts an electrode surface that contains an array of platinum domains on a gold substrate. This surface exhibits variable reactivity toward the hydrogen oxidation reaction as a result of the differences in catalytic activity of platinum and gold regions. Figure 4a is an optical microscope image of this metal electrode array, where the dark regions are platinum domains while the light regions are gold. Using hydrogen oxidation as the probe reaction, tip-sample feedback can be used to visualize catalytic activity via a local variation in tip current, which directly reflects changes in reactivity. A current map of this surface at open circuit (Fig. 4b) shows a large cathodic tip current at the platinum sites and low cathodic tip current at the gold sites, which is a direct measure of the differences in tip-sample feedback that reflects the local value of the hydrogen oxidation rate constant. A high tip current is measured above regions that exhibit a high rate constant for hydrogen oxidation ($k_{b,s}$) while a lower tip current is measured at regions with a small rate constant for that reaction. The variation in contrast from left to right in Fig. 4b is due, again, to sample tilt.

This SECM technique can readily be extended to examine more complex and technologically relevant electro-oxidation reactions. For example, the oxidation of methanol is an extensively studied

Figure 3. SECM images of normalized tip current over a $25\ \mu\text{m}$ diameter Pt-microelectrode disk sealed in glass in argon-purged $0.01\ \text{M}\ \text{H}_2\text{SO}_4/0.1\ \text{M}\ \text{Na}_2\text{SO}_4$ with the tip potential held at $-1.2\ \text{V}$. Two-dimensional SECM images at a tip-substrate separation of $10\ \mu\text{m}$ with substrate held at (a) $0.0\ \text{V}$ and (b) $1.1\ \text{V}$. The current scale is normalized with respect to the diffusion limited value (i_{∞}), with black indicating a large current value and white reflecting a small current. Image contrast has been discretized at normalized current level values of 0.05 to enhance differences in current.

Figure 4. Images of a chemically heterogeneous electrode comprised of an array of Pt disks on a Au substrate. (a) Optical image of Pt/Au array. The dark regions depict the Pt on a lighter Au substrate. (b) SECM image of Pt/Au array in $0.01\ \text{M}\ \text{H}_2\text{SO}_4$ and $0.1\ \text{M}\ \text{Na}_2\text{SO}_4$ when substrate is at open circuit.

reaction that represents a potentially viable liquid fuel for the anode reaction in a fuel cell.^{10,42,43} However, this reaction is fraught with difficulties involving incomplete oxidation and the formation of electrode deactivating intermediates associated with at least two parallel reaction pathways.¹⁰ Although platinum is a useful catalyst for the oxidative dehydrogenation of methanol, it quickly deactivates due to the adsorption of surface poisons. Figure 5a illustrates the substrate (top) and tip (bottom) response to cycling the potential of a platinum substrate in a solution containing 10 mM methanol with the tip probing the local proton concentration. At a tip-substrate separation of 100 μm (dashed line), the tip current is constant in a manner very similar to simple hydrogen oxidation (Fig. 2a). Under these conditions, the substrate current exhibits features characteristic of methanol oxidation. The hydrogen adsorption/desorption peaks at low potentials are reduced in this solution due to competition with adsorbed methanol. At more positive potentials, several regions of anodic current associated with methanol oxidation are observed. On the positive-going scan, methanol oxidation initiates at approxi-

mately 0.3 V before reaching a maximum at 0.5 V. The onset of this oxidation is generally attributed to the adsorption of water or hydroxide, which can serve to oxidize surface poisons. After this maximum, the current decreases due to thickening of the platinum oxide. During the reverse scan, methanol is again oxidized following the reduction of platinum oxide with a peak centered at 0.3 V.

The ability to monitor this reaction with the SECM is seen when the tip-sample separation is decreased to 2 μm (Fig. 5a, solid lines). A small increase in the oxidation current at the substrate electrode is observed. This additional anodic current can be attributed to a combination of hydrogen oxidation due to feedback with the tip and a reduction in the interfacial pH, which enhances the methanol oxidation reaction. At this separation, the tip response exhibits a variety of features. The tip current reflects the interfacial proton concentration, which is increased both by hydrogen oxidation due to positive feedback and also from the methanol oxidation reaction. Although CO_2 reduction is possible at the tip electrode, this process is not observed at the tip potentials used in this work. In particular, we observe no appreciable CO_2 reduction current at the tip in the presence of dissolved CO_2 under these tip potentials. At more negative tip potentials, it is likely that CO_2 will be detected. However, we have avoided those conditions in this work.

Two large peaks are observed in the tip response, which appear at potentials corresponding to the methanol oxidation peaks in the substrate current response. These peaks are thus attributable to protons generated from the methanol oxidation reaction. This current due to methanol oxidation is added to a background tip current that is due to feedback from the hydrogen oxidation reaction on the substrate. If only this background current is considered, large positive feedback is observed during the forward substrate scan at potentials below the onset of methanol oxidation (<0.3 V). If this region is compared to the response of pure platinum in sulfuric acid (Fig. 2a), it appears that rate of hydrogen oxidation in a methanol-containing solution under these solution and scanning conditions is large and similar to that for the pure platinum surface.

These results suggest that this methodology can be extended to characterize complex and multistep electro-oxidation reactions. In particular, the hydrogen probe reaction can be utilized in any reaction involving protons or hydrogen. In terms of complexity, interpretation of the SECM response toward the hydrogen oxidation reaction is relatively simple as variations in tip current can be related to either the adsorption/desorption of hydrogen or changes in the hydrogen oxidation rate constant. The case for methanol oxidation is considerably more complex as the tip can respond to changes in the substrates' hydrogen oxidation rate, surface deactivation, or from the additional protons generated by the methanol oxidation reaction. Ultimately, however, these issues can be properly addressed by careful experimental design and theoretical modeling.

Conclusions

This work demonstrates a unique and versatile application of the SECM that can achieve direct, performance-based evaluation of electro-oxidation catalysts. We are currently extending this methodology to characterize the influence of deactivating species for the hydrogen oxidation reaction, performing screening and characterization experiments on multicomponent catalyst samples created on compositionally graded surfaces, and characterizing reaction pathways in multistep dehydrogenation reactions through the use of additional surface and chemically sensitive probe reactions.

Acknowledgments

The authors would like to acknowledge the Office of Naval Research for a Young Investigator Award, the National Science Foundation for a Faculty Early Career Development Award, the Camille and Henry Dreyfus Foundation for a New Faculty Award, and the Donors of The Petroleum Research Fund as administered by the American Chemical Society, for partial support of this research. We also wish to thank Molecular Imaging Corporation for a Young Electrochemical Scanning Probe Microscopist Award.

Figure 5. (a) Response of Pt substrate (top) and SECM tip (bottom) at tip-sample separations of 100 μm (dashed line) and 2 μm (solid line) in 0.01 M H_2SO_4 /0.1 M Na_2SO_4 containing 10 mM methanol with the tip held at -1.2 V. (b) Schematic of tip-sample interface with reactions.

The University of Virginia assisted in meeting the publication costs of this paper.

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