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EXTENDED ABSTRACT

Impact of the spatial distribution of morphological patterns on the efficiency of electrocatalytic gas evolving reactions•

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Abstract: The efficiency of electrocatalytic gas evolving reactions (hydrogen, chlorine and oxygen evolution) is a key challenge for important industrial processes, such as chlor-alkali electrolysis or water electrolysis. The central issue for the aforementioned electrocatalytic processes is their huge power consumption. Experimental results accumulated in the past, as well as some predictive models ("volcano" plots) indicate that altering the nature of the electrode material cannot significantly increase the activity of the mentioned reactions. Consequently, it is necessary to find a qualitatively different strategy for improving the energy efficiency of electrocatalytic gas evolving reactions. A usually disregarded fact is that gas evolution is an oscillatory phenomenon. Given the oscillatory behavior, a key parameter of macrokinetics of gas electrode is the frequency of gas-bubble detachment. Bearing in mind that gas evolution greatly depends on the surface morphology, a methodology is proposed that establishes a rational link between the morphological pattern of an electrode with its activity and stability. Characterization was performed using advanced analytical tools. The frequency of gas-bubble detachment was obtained in the configuration of scanning electrochemical microscopy (SECM), while the corrosion stability was analyzed using a miniaturized scanning flow electrochemical cell connected to a mass spectrometer (SFC–ICPMS).

Keywords: energy efficiency; electrocatalysis; morphology; SECM; activity; stability.

Due to their technical importance, electrocatalytic gas-evolving reactions (hydrogen, chlorine and oxygen evolution) have been the subject of investigation for decades.[1–3] From well-established large scale industrial processes, such as chlor-alkali technology towards water electrolysis and electrochemical CO_2

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reduction, the efficiency of electrocatalytic gas evolving reactions (GER) has been a major challenge due to the large amount of electricity necessary to conduct electrode reactions at a desirable rate.[4] Energy efficiency in one electrochemical reactor is usually monitored by the voltage corresponding to the predefined turnover of product controlled by the imposed current intensity. An essential task is to minimize the overvoltage, which represents the difference between the actual voltage and the voltage in the state of equilibrium (reversible voltage).

The energy efficiency during one electrocatalytic process strongly depends on the design of the electrochemical interface. The functionality of an electrochemical interface is largely influenced by the nature of the material of the chosen electrode that belongs to the scope of electrocatalysis.[2] Electrocatalysis essentially deals with the impact of the electrode material on the rate of an electrode reaction. The predictive bases on which electrocatalysis rests are empirical or theoretical models known as "volcano" plots, in which the kinetics of the electrode reaction is expressed as a function of some catalytic descriptor, which is in fact some physicochemical property of the material (binding energy of intermediates, number of outer electrons, *etc*.).[5] The apex of "volcano" responds to the maximal kinetics, which is essentially determined by the optimal value of a catalytic descriptor (Sabatier Principle). For example, a noticeable fact is that RuO_2 is at the apex of the "volcano" plot for the oxygen evolution reaction (OER) and the chlorine evolution reaction (CER).[6,7] If a material whose activity responds to the maximum of the "volcano" plot is identified, the question that would naturally arise is: how to improve further the efficiency of the given reaction?

A high intrinsic activity of the chosen electrocatalyst, reflected by the high turnover per active site, however, goes hand in hand with a certain self-inhibiting effect. Namely, the phenomenon of supersaturation with the product is actually a prerequisite for the gas formation.[8,9] The formed gas-bubbles cover a fraction of the active surface area and induce additional overpotential. It is important to mention that the gas bubble effect was detected to be the major source of overpotential in a case of chlor-alkali technology.[2] Consequently, this issue requires serious investigations, which could be beneficial for all gas-evolving reactions, even for those that are not driven by the electrode potential. At the same time, electrode materials, especially those used as catalysts for anodic electrocatalytic reactions, are subjected to intensive corrosion.[10] The electrode materials used to catalyze the mentioned electrode reactions usually originate from the family of noble metal oxides. Considering that the price of noble metals is subject to unpredictable fluctuations (for example, the price of Ru jumped in 2007/2008 by 1000 %[11]), it is of major importance to find strategies to 1) stabilize electrocatalytic materials, 2) reduce the loading with noble metals and/or 3) replace noble metals with cheaper and more abundant materials.

A promising approach to address the above-mentioned issues is a rational design of the surface morphology. Namely, morphology has strong impact on the gas evolution (for example, it influences the contact angle at the triple phase boundary) and influences the utilization of the active surface area by determining the accessibility of active sites.[12] Additionally, expecting that high local overpotentials and current densities could enhance degradation of electrocatalysts,[13] it is essential to investigate to what extent the stability of electrocatalysts is influenced by the morphological pattern. State of the art anodes for the electrocatalytic gas evolution are DSA (dimensionally stable anodes)-type electrodes. Usually, “valve” metal-like titanium is coated with a mixed transition metal oxide. Catalytically, the active component is a noble metal-based oxide (for example ruthenium oxide), the long-term stability of which is assured by mixing with a “valve” metal-based oxide (for example titanium oxide). An important pre-condition for mixed oxide formation is that the parameters of the crystal lattice match (according to the Hume Rothery Rules).[14] A typical morphological pattern of DSAs, the so-called “mud-crack” structure, contains two interesting features, namely “islands” and “channels”, which could be potentially beneficial. The edges of the islands can allow high local activities, while the channels can contribute to mass transport by allowing certain internal hydraulic regimes *via* microconvection.

Two studies provide particularly interesting insights into the behavior of DSAs. Trasatti and co-workers derived a method to distinguish easily accessible “outer” surface area from the hardly accessible “inner” surface area (originating in nanopores, *etc*.).[15] In the mentioned work, the authors stated that only the outer surface is functional and accessible for the reaction. Simultaneously, Evdokimov reported that at very high current densities (up to 4 A cm^{-2}), the inner surface area starts to participate in the reaction.[16,17] The results of Evdokimov could be understood in terms of an increase of the interfacial overpressure, which allows solvent penetration towards the nanopores (according to the Young–Laplace Equation for capillary forces).[18] While Evdokimov was increasing the imposed intensity of the process (rate of reaction) at the analyzed electrode, the question was whether the opposite was possible. Namely, whether it is possible for the pre-defined intensity of the process to gradually change the morphology and cause activation of the inner surface area or at least increase its utility. To achieve better utility of surface area, it is important to bear in mind that gas evolution is an oscillatory phenomenon.[19] Thermal oscillations of the gas-bubbles cause periodic displacement of the surrounding liquid, which in return influences the root of the surrounding gas-bubbles and ultimately cause their detachment. The smaller the gas-bubbles are, the more frequently they oscillate and finally detach. Consequently, given the oscillatory behavior, a key parameter of the macrokinetics of a gas-evolving electrode is the frequency of gas-bubble detachment. In this sense, the goal was to find a way to generate gas-bubbles with small radius at electrode/electrolyte interface. Knowing that gas bubble evolution consists of three processes: 1) nucleation, 2) growth and coalescence and 3) detachment, it seems rational to design electrodes with adequate thickness of the catalyst layer and size of the "channels" so the gas bubbles can nucleate inside the "channels" that would limit their growth. In this respect, the thickness of the coating and size of the "channels" should be similar to the critical radius of gas-bubble nucleation.[20] To achieve the targeted pattern, the synthesis was based on controlling the tensile stress in the catalyst layer. The tensile stress delivered to the coating could be controlled by adequate thermal treatment (calcination temperature, rate of heating/cooling…) and by creating mismatch in the coefficients of thermal expansion between support and catalyst layer. In this sense, the "breakage" of the catalyst layer is under certain measures of control as is the size of the "channels". Besides the design of the morphological pattern, it was important to ensure that the desirable surface features are uniformly distributed over the surface.[21] While DSA coatings were usually synthesized using the thermal decomposition procedure, important progress was made through the introduction of sol–gel route, as shown by Nikolić and co-workers.[22] The sol–gel procedure allowed coatings to be obtain with significantly reduced surface inhomogeneities in the morphology and/or composition. Reducing surface inhomogeneities is already recognized as an important aspect of electrode design and as one of the potential strategies for further improvement of DSA performance.[23] Although, the impact of the spatial distribution of activity on electrode performance is still not adequately understood, it has been proven to be of major importance for efficient gas evolution.[21]

Besides the design of the features of the electrode surface, of major importance is simultaneously to have a realistic insight into the catalytic performance of a particular material, which further strongly depends on the employment of adequate analytical tools and procedures. Particularly important was to characterize and adequately interpret gas-bubble evolution. The frequency of gas bubble detachment at various potentials was monitored using scanning electrochemical microscopy (SECM).[24] This is the first work in which an SECM setup was adopted for the characterization of GER by recording potential dependent frequency spectra. From the recorded spectra, the point of transition from pseudo-periodical to periodical behavior could be detected, which was related with a drop in the efficiency. All the tested DSA coatings for which a characteristic frequency of the gas-bubble detachment could not be estimated exhibited relatively low activity. This could be related to the spatial distribution of the activity, which can also be visualized *in situ* using SECM.[21,25] Finally SECM in combination with cyclic voltammetry (CV) was used for the most challenging task, namely to develop a methodology that quantifies what fraction of the catalyst layer (what percentage of overall active sites) really participate in the reaction in dependence on the applied potential. Finally, as a part of an analysis of catalyst stability, time resolved dissolution profiles were recorded using a recently developed setup based on the coupling of electrochemistry with mass spectrometry (SFC–ICPMS).[26,27] From the dissolution profiles, it was clear that the more active sample, due to the morphological pattern that promotes efficient gas evolution and assures a larger effective surface area, at the same time could be more stable, which is of major importance on a technical scale.

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ИЗВОД

УТИЦАЈ ПОВРШИНСКЕ МОРФОЛОГИЈЕ НА ЕФИКАСНОСТ РЕАКЦИЈА СА ИЗДВАЈАЊЕМ ГАСА

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Ефикасност електрокаталитичких реакција са издвајањем гаса (издвајање водоника, хлора и кисеоника) је кључни изазов за важне индустријске процесе као што су хлор–алкална електролиза или електролиза воде. Централни изазов за наведене електрокаталитичке процесе је огромна потрошња електричне енергије. Експерименталне чињенице акумулиране током претходне четири деценије, као и неки важни експериментални и теоретски модели ("вулканске" криве) указују да мењање природе електродног материјала не може битно увећати активност поменутих реакција. Сходно томе, неопходно је пронаћи квалитативно другачији приступ за побољшање енергетске ефикасности електрокаталитичких реакција са издвајањем гаса. Чињеница која се обично занемарује јесте да је издвајање гаса осцилаторни феномен. С обзиром на осцилаторно понашање, кључни параметар макрокинетике гасних електрода јесте фреквенција издвајања мехурова гаса. Имајући у виду да издвајање гаса у великој мери зависи од површинске морфологије, предложена је методологија која успоставља рационалну везу између морфологије електроде и њене активности и стабилности. Карактеризација је извршена коришћењем модерних аналитичких метода. Фреквенција издвајања гаса је добијена у конфигурацији скенирајуће електрохемијске микроскопије (SECM) док је корозиона стабилност анализирана уз помоћ минијатуризованог проточног електрохемијског реактора повезаног са масеним спектрометром. (SFC–ICPMS).

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