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EXTENDED ABSTRACT

**Contemporary approaches in development of new materials for electrochemical energy conversion\***

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*Abstract:* The development of modern society is followed by increasing energy demands, highlighting the importance of sustainability of the energy system. In line with this task, electrochemistry has been set in the centre of modern research, offering a large number of solutions for energy conversion and storage. One of the main problems is the identification of new electrocatalytic materials which are used for energy conversion applications. A brief view on the use of modern computational techniques in discovery of new electrocatalysts is provided, mainly focusing on the electronic structure methods and the idea of catalytic descriptor. Using this approach, it is possible to screen many candidates for new electrocatalysts. However, the complexity of an electrified interface requires additional efforts to fully understand the properties of electrocatalytic materials.

*Keywords:* electrocatalysis; materials design; electronic structure methods; activity descriptor.

INTRODUCTION

Our society is addicted to energy. With growing demands, the necessity to build a sustainable, decentralized energy grid comes to reality. One of the prerequisites to achieve this goal is to develop efficient energy conversion and storage systems which can respond to different needs of many types of users. Electrochemistry, being the science of conversion of electrical into chemical energy and *vice versa*, is a natural approach to solve many of these challenging issues. For a long time electrochemistry describes different types of chemical power sources. While electrochemical capacitors, batteries and fuel cells differ by energy and power density (in many ways being complementary to each others),

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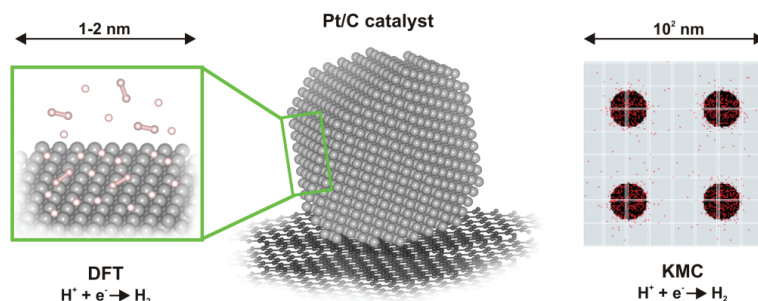
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our everyday life, concerning mobile applications, usually runs on batteries. However, electrocatalysis is known as one of the pillars of sustainable energy development. It is the central part of fuel cell technologies, hydrogen economy, and numerous industrial processes due to high selectivity, simple control over the reaction rates and easy scale up. While the performance of a fuel cell depends on many factors, its core component is the catalyst. Taking for example the proton exchange membrane fuel cell (PEMFC), the anodic reaction is hydrogen oxidation (HOR), while the cathodic reaction is oxygen reduction reaction (ORR). As a result, gaseous  $H_2$  and  $O_2$  are converted to  $H_2O$ , while electricity and heat are obtained. In order to proceed at acceptable rates, both reactions require properly chosen electrocatalyst and the magic starts with platinum and other metals located close to it in the periodic table of elements (PTE). Along with this magic, a painful truth comes to its way – the prices of these metals are very high and their global reserves are rather small. Hence, in order to bring this technology to everyday use one has to reduce the price of the catalyst and preserve its activity, or increase the activity, enabling the reduction of the amount of the catalyst.

It is relatively easy to search for new electrocatalytic materials. One can simply take the entire PTE, remove noble gasses and radioactive elements, leaving approx. 80 elements, and then combine them as nature allows. However, such a quest is not reasonable to start. By using some common knowledge number of candidates can be reduced by proper choice of the starting point, but this still remains a task which cannot be completed at the rate requested by technological and economic growth. In order to search for new electrocatalytic materials a complex multiparametric space containing many different parameters related to chemical and physical properties of electrocatalysts and their performance has to be significantly reduced. This brings us to the idea of a catalytic descriptor – a single parameter (property) of an electrocatalyst which can be linked to the catalytic activity in a unique way. Maybe the best known example is the hydrogen–metal bond strength (or metal hydride formation enthalpy change) which is used as the descriptor of electrocatalytic activity towards hydrogen evolution reaction.<sup>1</sup> Although being both embraced and criticised,<sup>2,3</sup> this approach is justified in the spirit of Sabatier principle, which is a long standing paradigm in heterogeneous catalysis (and electrocatalysis can be considered as a special type of heterogeneous catalysis). As the electronic structure methods in computational chemistry and physics have reached outstanding levels of accuracy, the use of theoretical approach in the search for new electrocatalytic materials is natural and the most frequently used techniques are those based on density functional theory (DFT). These techniques allow the analysis of a vast number of possible candidates, assuming that we know what we are looking for, and a shift from traditional trial-and-error approach to rational design. Hence, if the value of a given descriptor can be calculated, the proper candidates for new electrocatalyst can be

identified and then tested in the lab. Many examples of such screening studies and theory-guided discovery of new electrocatalysts can be found in the literature.<sup>4-6</sup> However, we must note that the electrochemical systems are very complex and that rather special, or more precisely extreme, conditions exist at an electrified interface. Although significant efforts have been invested to develop first principles electrochemistry (FPEC),<sup>7</sup> a complete computational framework is still missing. Hence, a large fraction of scientific community in this field currently works with catalytic descriptors and additional schemes to include electrode potential into the picture, the most popular one being the computational hydrogen electrode<sup>8</sup> approach. In our view, the use of catalytic descriptors for electrochemical reactions is safe (but should be taken with care) if a descriptor is identified by a combination of reliable experimental data on model systems and *ex situ* determined properties of the catalysts (like adsorption energies, work functions and so on). Moreover, we emphasize that the true strength of computational techniques is in the understanding the reactivity trends, which compares well with the practices in experimental electrocatalysis. When this is combined with some general relationships regarding surface chemistry, like scaling relations,<sup>9</sup> and strain dependence of relevant surface properties in layered electrocatalysts,<sup>10</sup> revealed using theory, many possible candidates and their specific architectures can be screened without employing computations at all.

While electronic structure methods like DFT can easily cope with relatively small systems (< 1 nm), we note that realistic electrocatalysts are usually in the form of supported nanoparticles. Even for the most powerful supercomputers a nanoparticle containing several thousands of atoms is a difficult task. In order to address spatial and temporal domains beyond the limits of electronic structure methods other computational approaches are used, like Kinetic Monte Carlo (KMC).<sup>11,12</sup> We briefly summarize how DFT and KMC “see” catalyst along with spatial scales addressed with these two approaches in Scheme 1. While these techniques require input from the experiment or higher-level theory, a lot of important information can be obtained, particularly relating to the kinetics of elec-



Scheme 1. Modelling of hydrogen evolution reaction on Pt/C catalyst considering spatial scales accessible by DFT and KMC.

trocatalytic reactions, time evolution of electrocatalytic systems and the support-catalyst interplay.

Above presented view presents a small part of a complex mosaic related to the development of new electrocatalytic materials. We note that this picture puts the emphasis on the computation-aided development of new materials and it is the author's view on the current practice in the field. However, one should always keep in mind the complexity of electrified interface. We believe that the further developments of FPEC will bring more exciting strategies to address the electrocatalyst activity, selectivity and stability and open new horizons in discovering new electrocatalytic systems.

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ИЗВОД  
САВРЕМЕНИ ПРАВЦИ У ИСТРАЖИВАЊУ НОВИХ МАТЕРИЈАЛА ЗА  
ЕЛЕКТРОХЕМИЈСКУ КОНВЕРЗИЈУ ЕНЕРГИЈЕ

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Развој модерног друштва праћен је повећаним захтевима за енергијом, уз наглашавање важности одрживости енергетског система. У складу са овим задатком, електрохемија се нашла у центру савремених истраживања, нудећи велики број решења за конверзију и складиштење енергије. Један од главних проблема је идентификација нових електрокаталитичких материјала са применом у конверзији енергије. Приказан је кратак преглед употребе савремених рачунских техника у откривању нових електрокатализатора, фокусирајући се на методе базиране на електронској структури и коришћењу идеје каталитичког дескриптора. Користећи овај приступ могуће је испитати велики број потенцијалних кандидата за нове електрокатализаторе. Међутим, сложеност наелектрисане границе фаза захтева додатне напоре како би се у потпуности разумела својства електрокаталитичких материјала.

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