Over the past few decades, low-temperature fuel cells have undergone rapid development delivering prototypes and commercially available cars with impressive performance. The achievements and progress of the fuel cell research and development have been enthusiastically embraced by the transport industry boosting public and governmental interest and support. Besides polymer electrolyte membrane fuel cells (PEM FCs) based on hydrogen fuel, the direct alcohol fuel cell (DAFC) based on liquid fuels, such as methanol, ethanol and formic acid (alcohol fuels) have been viewed as possible power systems for portable electronic devices. In spite of the considerable progress, commercially competitive fuel cell cars and technology are still hindered by performance limitations and the high cost of Pt catalysts. Development of nanoscale bimetallic catalysts with low content of Pt and Pt-group metals exhibiting enhanced activity, and better stability than the pure metal has been pursued actively as the most promising strategy to make future advances.

Pt-bimetallic systems comprise of nanoscale structures of Pt in contact with another metal. Some of the examples, shown in Figure 1, include Pt-nanoclusters (sub-ML) on top of another metal, strained Pt monolayers and ultrathin films (over layers on top of another metal or alloys), Pt-alloys and Pt-alloy overlayers (random alloys and intermetallics). Besides the low content, a combination of Pt with another metal at nanoscales often result in the catalysts with superior activity compared to the single metal components. The reduced dimensionality coupled by geometric (ensemble effect) and electronic (ligand) effects can substantially alter the Pt activity. Real-world fuel cell catalysts (such as nanoparticles on carbon support) are complex and often it is hard to decouple different aspects that contribute to the catalytic activity and performance such as size, shape, and composition. For that reason catalytic reactions are best studied on well-defined single crystal surfaces, the so called model systems (Figure 1). Single-crystal metal electrodes have a special place in the field of electrochemical surface science and electrocatalysis. They have been essential for shaping our fundamental understanding of the processes and structure-reactivity relationship. The use of single-crystal vicinal surfaces enabled decoupling of electronics and surface structure effects resulting from the crystallographic orientation alone, and structural features such as terraces, steps, and kinks. Single crystal model systems have been essential for developing our understanding of the kinetics and mechanisms of electrocatalytic reactions providing an invaluable support for theoretical models and analysis (i.e., DFT, MD calculations). Without model system it would have been impossible to establish links between the bulk surfaces and nanoscale effects of size and shape.

Electrodeposition of Pt-Bimetallic Surfaces

Electrodeposition of electrocatalysts has an advantage in contrast to other chemical and physical, synthesis routes. Electrochemical routes are inexpensive and readily accessible; they are attractive because of their versatility, simplicity and easy scalability on electrodes of various shape and sizes ideal for a number of fundamental and practical studies. Moreover, they are an effective way of making clean surfaces, i.e., free of capping agents and organic molecules often used in the chemical synthesis methods, thus providing an ideal platform for studying electrocatalytic reactions on single crystals as well as on mesoporous nanocomposite electrodes.
Controlled epitaxial deposition of Pt is a challenge. Due to the very high surface energy and low diffusivity, Pt growth, regardless of the method of deposition, is non-uniform and proceeds via 3D island formation (Volmer Weber growth).\textsuperscript{12,14} The electrodeposition community has been actively pursuing different strategies and conditions for epitaxial films and alloy deposition, as reviewed next.

The SLRR Method

The surface limited redox replacement (SLRR) deposition method enabled for the first time successful epitaxial deposition of Pt films and nanoclusters with atomic scale control,\textsuperscript{15-18} on to other metal surfaces. Very quickly the method has become one of the most exploited to design 2 dimensional and nanoparticle Pt-bimetallic systems.

The SLRR method has been outlined elsewhere in this issue and utilizes the galvanic replacement of an underpotentially deposited (UPD) epitaxial metal layer, such as Cu and Pb, by a more noble metal such as Pt. The electrochemical surface science studies of UPD processes on single crystal surfaces over four decades\textsuperscript{20} provided a wealth of information about the epitaxial nature, thermodynamics and kinetics aspects of these and many other UPD processes. The UPD processes have been now used as fine tools for surface characterization (area, structure and composition) of complex systems,\textsuperscript{21-25} as well as enablers to grow and design thin films and alloys.\textsuperscript{15,18,26-32}

From the first demonstration of 2D deposition of a Pt monolayer, Cu UPD\textsuperscript{15} has now become the most commonly used sacrificial layer to design highly active Pt-monolayer catalysts,\textsuperscript{26,28} as well as functional nanoporous fuel cell electrodes.\textsuperscript{34,35} Further demonstration of the SLRR controlled deposition of Pt films has been done using Pb UPD\textsuperscript{18,19} as an excellent alternative for the comparative studies of the nature of UPD layer on the replacement kinetics, deposit structure and high deposition yield. Furthermore, the H UPD\textsuperscript{36} based Pt deposition has been shown on a proof of concept level and quickly extended to other Pt-group metals such as Pd well known for its unique H-sorption behavior.\textsuperscript{37,38} The coverage of deposited Pt in each SLRR cycle is generally defined by stoichiometry of the redox reaction, replacement reaction kinetics and structure of the UPD layer.\textsuperscript{39,40}

Experimental Configurations

There are different experimental configurations by which SLRR protocol can be conducted: 1) by electrode immersion and transfer between the cells containing the UPD metal ions and the second one with Pt-ion complex for the replacement reaction;\textsuperscript{15} 2) by exchanging the two solutions in the flow-cell set up;\textsuperscript{31} and 3) by the controlled deposition in a single-cell configuration,\textsuperscript{18} where growth of Pt films is maintained from the same solution containing both Pt and UPD-sacrificial metal ions\textsuperscript{18} with concentrations and the potential control optimized to avoid co-deposition of Pt during UPD metal formation step and avoid UPD metal incorporation during the replacement step.

Each configuration has advantages and disadvantages for the design of different Pt-bimetallic systems. The design of Pt-nanoclusters and monolayer catalysts (0 – 1 ML) can be best achieved by the immersion and transfer method with special care given to the control of the oxygen-free environment to prevent oxidation of UPD layer. Either by conducting deposition in a glove-box or using custom designed set-ups\textsuperscript{41} a secure transfer of stable and uncompromised UPD covered electrode can be achieved.

For deposition of multi-layered thin films of Pt, the automated flow-cell and the single-cell configuration (\textit{Ed. Note: See also companion article by Dimitrov et al. in this issue.}) offer easier control, and handling, but they require careful optimization of the conditions and monitoring of the potential changes during process. For illustration, the single-cell approach requires the metal ions concentrations and the control of the potential limits, to be optimized to maintain growth of high quality Pt, with minimum possible electrodeposition of Pt during UPD metal formation step and minimum possible UPD metal incorporation.\textsuperscript{18} The single-cell approach illustrated in Fig. 2 requires controlled application of the elemental SLRR steps: (1) a potential step typically of few seconds duration to form UPD sacrificial layer at negative potential limit $E_1$ followed by (2) an open circuit potential (OCP) galvanic displacement by a more noble Pt ions monitored in time and terminated at the potential corresponding to a UPD-free surface of the growing film, $E_2$ (positive potential limit). Moreover, by limiting the potential of the replacement reaction to value $E'_2$; $E_{1}^{\text{red}} < E'_2$ can be exploited for deliberate incorporation of the UPD sacrificial metal and design of nanoalloys.\textsuperscript{42}

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**Fig. 2.** Schematics of the SLRR protocol of Pt and Pt-Pb alloy deposition in the single-cell configuration using Pb UPD.
Pt-Bimetallic Model Systems for Electrocatalysis

So far the SLRR method has been used in many fundamental studies to design and study various catalytic reactions. Separating the contributions of the two key mechanisms of modification of the chemical properties of surfaces (geometric and ligand effects) is often very difficult because they usually occur together. Firstly, the activity of Pt can be altered by strain, i.e., by changing the average bond lengths between the Pt atoms in the supported ultra-thin layers on different substrates. Also, bonding interactions between the surface atoms of Pt and the substrate result in modification of the Pt electronic structure (ligand effect) therefore can change its surface catalytic properties. Here we would like to draw attention to a few systematic approaches oriented toward understanding of general trends in electrocatalysis by systematic variations of the structure of the Pt surface using SLRR method. Interested readers may also find more details and information in a recent review by Dimitrov.43

Pt films (overlayers) Epitaxial monolayers of Pt deposited via SLRR of Cu UPD on different single crystal surfaces such as Au(111), Rh(111), Pd(111), Ru(0001), and Ir(111)28,44 have been used as model systems to explore the effect of strain on the kinetics of reactions such as the oxygen reduction reaction, methanol oxidation, ethanol oxidation (EOR), and formic acid oxidation. The established experimental trends were used in combination with DFT calculations to rationalize to what extent changes in the average bond length of Pt-Pt (strained on the substrates with different lattice spacing) affect the kinetics rate and/or selectivity of the complex reactions with different pathways.

Another way to explore the effect of strain on Pt electrocatalytic properties is to vary the thickness of Pt films. Repeated application of SLRR cycles using UPD layers of Cu or Pb have been shown to produce epitaxial films of controlled thickness but with different roughness dependant on the stoichiometry and kinetics of the redox replacement reaction.34,45 For example, the studies of thickness dependant CO electrooxidation showed that besides strain in the layer, the morphology and roughness of the deposited Pt films play an important role in the potential shift, i.e., the strength of CO adsorption.45,46

Pt-nanoclusters (sub-ML) Two dimensional Pt nanoclusters at sub-ML coverage (0 ≤ 1 ML) on different substrates are ideal for studies of coverage dependant electrocatalytic behaviour. A recent study of Pt sub-ML on Au(111) grown by SLRR of Cu UPD showed that the kinetics of hydrogen oxidation reaction (HOR)47 is dependent on the size of Pt clusters (smaller clusters being less active for HOR), Fig. 3. The results were rationalized by average active strain in Pt nanoclusters that has two contributions: the tensile strain due to epitaxial misfit (4%) and the compressive strain due to the clusters finite size. Agreement with the DFT-derived model of the size-dependent strain indicates that the morphology/size of Pt-nanoclusters can be exploited to fine tune Pt activity on different substrates. The coverage dependant studies of CO electrooxidation on the overall activity and product distribution of the EOR.48,49

Pt nano alloys Nanoalloys are even more challenging systems as the effects of the surface structure and chemical composition equally shape Pt electrocatalytic behaviour. Studies on single crystal surfaces of Pt alloys and Pt- intermetallics50,51 have been extremely valuable but they are limited. Alloy single crystal surfaces are not easily grown and in some cases not available. The SLRR based deposition is one of the most promising pathways to controllably grow model 2D nanoalloy systems and study their properties. This is one of the least explored applications of SLRR method but one that could potentially have high impact.

So far three different approaches have been explored to grow nanoalloy films: 1) the galvanic replacement of a UPD metal later in the solution with both Pt and alloying metal mixed in a desired concentration ratio52,53 (examples include Pb UPD based growth of and Pt0.8X0.2 monolayers on Pd(111) surface where X = Ir, Ru, Rh, Pd, Au, Re, or Os); 2) the alternation of the replacement cycles of Pb UPD between separate solutions of Pt and Ru using flow-cell set up54 (alloys of different compositions 70:30, 82:28, and 50:50 were grown by controlling the number of alternating replacement cycles in Pt and Ru solutions); and 3) controlled incorporation of the sacrificial Pb UPD metal during Pt deposition to form PtPb alloys (up to 10% Pb composition) by controlling the potential of the replacement step. In the last case of PtPb alloys it has been shown that Pb has a strong screening effect on the adsorption of both H and CO. The changes in alloy composition cause a negative shift in the potential of the peaks of CO oxidation (weaker CO bond) that scales with the increase of Pb content. The results suggest electronic and bifunctional effects of incorporated Pb on the electrochemical behaviour of Pt.

(continued on next page)

![Fig. 3.](image_url) Normalized exchange current density for HOR on Pt sub ML on Au (111) as a function of: a) mean size of Pt clusters population and B) average active strain calculated for Pt clusters with size corresponding to the mean of Pt clusters’ population for each Pt sub-ML coverage on Au(111). Reprinted by permission from Springer Nature and Copyright Clearance Centre: Springer, Ref [47]. Copyright (2012).
What Is in the Future?

The SLRR based approaches will undoubtedly play an important role in the future of fuel cell development and electrocatalysis in general. Control of the structure, thickness and composition on atomic scales provides an excellent platform for model studies on different types of bimetallic systems. In combination with theoretical modelling, the systematic design and studies of various systems will enable the development of more powerful and stable catalysts with tailored electrocatalytic properties. It can also contribute to the understanding of other equally important aspects of the ideal catalysts such as durability. In this vein, recent studies have shown that SLRR grown films and structures are ideal systems to study Pt-dissolution during different catalytic reactions.55,56

In this article the focus was on Pt-electrocatalysts for fuel cell applications as the SLRR method has made the biggest impact in this area. The potential and challenges, of extending the approach to the design of other (both noble and transition) bimetallic systems of interest, are exciting. Some of the active areas of research include improving the activity and selectivity of bimetallic catalysts for carbon dioxide electrochemical reduction, environmental and water cleaning, and sensing. Design of multilayers and 2D nanoslabys (particularly those with no bulk counterparts) with controlled composition and distribution of components, can open new avenues of interest beyond the field of electrocatalysis such as nanophotonics, corrosion and microelectronics. The future is bright indeed.

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