

Fundamentals of Underpotential Deposition : Importance of Underpotential Deposition in Interfacial Electrochemistry

Jong-Won Lee and Su-Il Pyun[†]

*Corrosion and Interfacial Electrochemistry Research Laboratory at Department of Materials Science and Engineering,
Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong,
Yusong-Gu, Taejeon 305-701, KOREA*

(Received September 14, 2001 : Accepted October 30, 2001)

Abstract. This article covers the fundamentals of underpotential deposition (UPD), focussing on the importance of UPD in interfacial electrochemistry. Firstly, this article described the basic concepts of UPD, including underpotential shift and electrosorption valency. Secondly, the present article explained UPD of hydrogen, followed by hydrogen evolution or hydrogen absorption, giving special attention to the adsorption sites of hydrogen on metal surface and the absorption mechanism into Pd. Finally, this article briefly presented the important factors associated with UPD in various fields of interfacial electrochemistry from practical viewpoints.

초 록 : 본 논문은 계면 전기화학에서의 underpotential deposition (UPD)의 중요성에 초점을 맞추어 UPD의 기본 원리에 대하여 다루었다. 우선 underpotential shift와 electrosorption valency에 대한 설명과 함께 UPD의 기본개념을 기술하였다. 다음으로 금속표면에서의 수소발생 또는 금속내부로의 수소흡수 반응 이전에 관찰되는 수소의 UPD를 설명하였고, 특히 금속 표면에서의 흡착위치와 Pd으로의 흡수기구에 대하여 중점적으로 기술하였다. 마지막으로, 계면 전기화학의 여러 분야에서 UPD와 관련된 중요한 인자들을 응용적인 측면에서 간략히 설명하였다.

Key words : Underpotential deposition, Overpotential deposition, Underpotential shift, Electrosorption valency, Hydrogen, Palladium

1. Introduction

Underpotential deposition (UPD) is one of the most interest subjects within the frame of interfacial electrochemistry, which has been attracting the attention of both scientists and engineers for a long time. Since the systematic experimental studies on UPD of metals by Lorenz et al.^{1,2)} in the 1970's, knowledge of thermodynamic and kinetic properties of UPD in various substrate/adsorbate systems has been accumulated by numerous researchers. Especially, a significant progress in the theory of UPD has been made by Kolb and coworkers,^{3,4)} who first introduced the concept of underpotential shift in order to describe the thermodynamic properties of UPD. The basic ideas of UPD have proven to be helpful for an understanding of the principles underlying the electrosorption, the electrocrystallisation, the electrocatalysis and many other phenomena. Recently, studies on UPD of hydrogen have led to considerable advance in the development of metal-hydride secondary batteries and hydrogen-based fuel cells.

The objective of this article is to overview the fundamental aspects of UPD. For this purpose, we firstly presented the phenomena of UPD, giving an example of Pb/Au system which is considered as a good benchmark, and also described the concepts of underpotential shift and electro-

sorption valency. Secondly, we gave the detailed discussion on UPD of hydrogen, emphasising the adsorption sites of hydrogen on metal surface and the absorption mechanism into Pd. Finally, we shortly explained the importance of UPD in electrocrystallisation, electrocatalysis and electrochemical supercapacitors from practical points of view.

2. Fundamentals of Underpotential Deposition

2.1. Basic concepts of underpotential deposition

In order to cathodically deposit Pb on the same bulk metal from a solution containing Pb ions, one has to apply potentials negative to the reversible electrode potential of the Pb^{2+}/Pb couple in that solution, that is, an overpotential should be given. This process is denominated "overpotential deposition (OPD)", which needs a more useful work. However, when the substrate is replaced by a different metal, e.g. Au, the cathodic deposition of Pb is observed at potentials positive to the reversible electrode potential.

Fig. 1 shows the cyclic voltammogram measured on the Au electrode in 0.1 M HClO_4 solution containing 0.1 mM $\text{Pb}(\text{ClO}_4)_2$ with a scan rate of 10 mV s^{-1} . This figure was reproduced from the result by Deakin and Melroy.⁵⁾ During the scanning of the applied potential from 0.4 to -0.55 V(SCE) in the cathodic direction, two current peaks denoted as UPD-1 and UPD-2 appear in the potential ranges 0.1 to

[†]E-mail: sipyun@mail.kaist.ac.kr

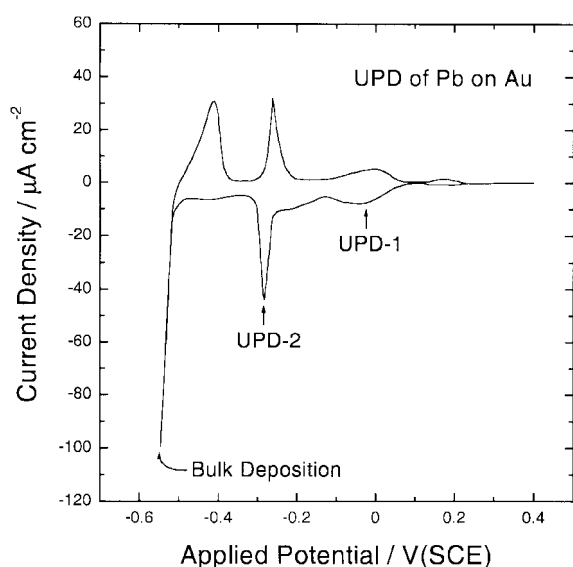


Fig. 1. The cyclic voltammogram obtained from the Au electrode in 0.1 M HClO₄ solution containing 0.1 mM Pb(ClO₄)₂ with a scan rate of 10 mV s⁻¹.⁵⁾ UPD-1 and UPD-2 represent the current peaks due to the underpotential deposition of Pb on the Au electrode.

-0.1 V (SCE) and -0.2 to -0.3 V(SCE), respectively, before the bulk deposition of Pb below -0.5 V(SCE). Both current peaks of UPD-1 and UPD-2 are assigned to the deposition of Pb on the Au electrode, and the charge determined by the integration of these current peaks corresponds to that for the deposition of a monolayer of Pb on that electrode. The above phenomenon is referred to as “underpotential deposition (UPD)”, because it occurs at potentials positive to the reversible electrode potential for the bulk deposition, namely, under the application of underpotential. This process needs a less useful work.

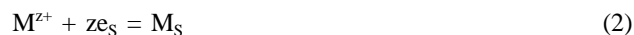
Generally, UPD is defined as the electrochemical formation of non-bulk surface layer at potentials positive to the reversible electrode potential for the bulk deposition of the adsorbate. However, it should be noted that UPD is a rather general phenomenon observed in anodic reaction as well as cathodic reaction. For example, UPD of oxygen^{6,7)} takes place at potentials negative to the reversible electrode potential for oxygen evolution reaction as an anodic oxidation, which is similar to UPD of hydrogen.

2.2. Underpotential shift

The underpotential shift has been used as a way of characterising UPD, which is closely related to thermodynamic and physical quantities such as chemical potential, work function and binding energy. The underpotential shift was defined originally by Kolb et al.^{3,4)} as the difference in potential between the current peak due to the desorption of a metal M adsorbed on a foreign substrate S and that peak corresponding to the dissolution of the pure metal M. In later, Leiva⁸⁾ has generalised the concept of the underpotential shift as follows: the equilibrium potential of the substrate(S)/adsorbate(M) system at a given degree of coverage by the adsorbate, measured with respect to an electrode of the metal

M, both in equilibrium with the same solution containing dissolved ions of M^{z+}.

As the first step towards a systematic theoretical study on UPD, Kolb et al.^{3,4)} have derived the relationship between the underpotential shift and the chemical potential, considering the following reactions:



Here, the reactions (1) and (2) represent the deposition processes of M^{z+} ion on the same metal M and on the foreign substrate S, respectively. Applications of the condition for electrochemical equilibrium to the reactions (1) and (2) yield

$$\eta_{M^{z+}} + z\eta_{e_M} = \eta_{M_M} \quad (3)$$

$$\eta_{M^{z+}} + z\eta_{e_S} = \eta_{M_S} \quad (4)$$

respectively, where η_k denotes the electrochemical potential of the particle species k. Since the M^{z+} ions in the reactions (1) and (2) are assumed to be in equilibrium in the same solution, their electrochemical potentials, $\eta_{M^{z+}}$ in Eqs. (3) and (4), should be the same. By combining Eqs. (3) and (4) using the relation $\eta_k = \mu_k + ze\phi^\alpha$ (phase $\alpha = M$ or S), the following expression for the underpotential shift $\Delta\phi_{UPD}$ can be obtained:

$$\Delta\phi_{UPD} = \frac{1}{ze}\Delta\mu_{M/S} = \frac{1}{ze}(\mu_{M_M} - \mu_{M_S}) \quad (5)$$

where e is the electronic charge, and μ_{M_M} and μ_{M_S} represent the chemical potential of the metal atom M adsorbed on itself and the chemical potential of the metal atom M adsorbed on the foreign substrate S, respectively. Note that μ_{M_S} is a function of coverage by the adsorbed metal atom M. Eq. (5) clearly shows that the underpotential shift $\Delta\phi_{UPD}$ is linearly correlated to $\Delta\mu_{M/S}$. Schmickler⁹⁾ has also derived the above relationship between $\Delta\phi_{UPD}$ and $\Delta\mu_{M/S}$ by employing thermodynamic cycle.

The fact that the underpotential shift has a mutual relationship with the work functions of substrate and adsorbate has been disclosed experimentally by Kolb and coworkers.³⁾ In the study on the UPD of several substrate/adsorbate couples in aqueous and non-aqueous solutions, they have plotted the underpotential shift $\Delta\phi_{UPD}$ against the difference in work function between substrate and adsorbate $\Delta\Phi_{M/S} = \Phi_S - \Phi_M$, and have found a linear relationship between $\Delta\phi_{UPD}$ and $\Delta\Phi_{M/S}$ with a slope of 0.5 V eV⁻¹. Assuming that the bonding character between substrate and adsorbate is fully ionic when coverage by the adsorbate is approximated to zero, Trasatti¹⁰⁾ has theoretically obtained the following relationship between $\Delta\phi_{UPD}$ and $\Delta\Phi_{M/S}$:

$$\Delta\phi_{UPD} \approx \frac{1}{e}\Delta\Phi_{M/S} = \frac{1}{e}(\Phi_S - \Phi_M) \quad (6)$$

In a recent theoretical work on UPD, Sánchez and Leiva¹¹⁾ have predicted a linear relationship between the underpotential shift $\Delta\phi_{UPD}$ and the difference in binding energy $\Delta E_b(M/S)$,

with the aid of a first-principles calculation based on density functional theory:

$$\Delta\phi_{\text{UPD}} \approx \frac{1}{ze} \Delta E_b(\text{M/S}) = \frac{1}{ze} [E_b(\text{M-M}) - E_b(\text{M-S})] \quad (7)$$

where $E_b(\text{M-M})$ and $E_b(\text{M-S})$ mean the binding energy between atoms in pure metal M and that energy between adsorbed metal atom M and substrate S, respectively. Consequently, from the above results obtained with some thermodynamic considerations, it is noticed that the underpotential shift provides the valuable information on the necessary conditions for the occurrence of UPD and the binding characteristics between two substances involved in that process.

2.3. Electrosorption valency

The electrosorption valency describes the charge flow during electrosorption reaction.¹²⁻¹⁴ That is, it represents the charge required for the following UPD process at a constant potential:



Here, γ is the electrosorption valency, and the structure of the double layer and the adsorption/desorption of water molecules are ignored. The value of γ can vary between 0 and z , depending on the orientation of the adsorbed layer or the substrate surface.⁵

The electrosorption valency γ is determined by a ratio of the charge passed during the UPD process to coverage by the adsorbate. The methods for measurement of coverage by the adsorbate include radiotracer technique and electrochemical methods such as cyclic voltammetry.¹³ In addition, electrochemical quartz crystal microbalance (EQCM) technique is useful for evaluating coverage by the adsorbate, since it allows the direct measurement of the mass of the adsorbed atoms during the UPD process.^{5,14-16} The general topic of electrosorption and the experimental methods used for the determination of electrosorption valency have been reviewed by Schultze and Koppitz.^{13,14}

3. Underpotential Deposition of Hydrogen

3.1. Overpotential deposition and underpotential deposition of hydrogen

The mechanism of hydrogen evolution in aqueous solution involves the formation of an adsorbed hydrogen atom (Volmer adsorption), an electrochemical desorption of hydrogen into solution (Heyrovsky desorption) and a chemical desorption by the combination of two adsorbed atoms (Tafel desorption).¹⁷⁻¹⁹ Among these reactions, the Volmer adsorption corresponds to the OPD of hydrogen at potentials negative to the reversible electrode potential for hydrogen evolution reaction E_{HER} , which is measured to be 0 V with respect to a reversible hydrogen electrode (RHE). This overpotentially deposited hydrogen (H_{OPD}) acts as an intermediate in the subsequent hydrogen evolution reaction.

Since the first recognition of UPD of hydrogen on a Pt surface by Frumkin and Slygin,^{20,21} it has been extensively

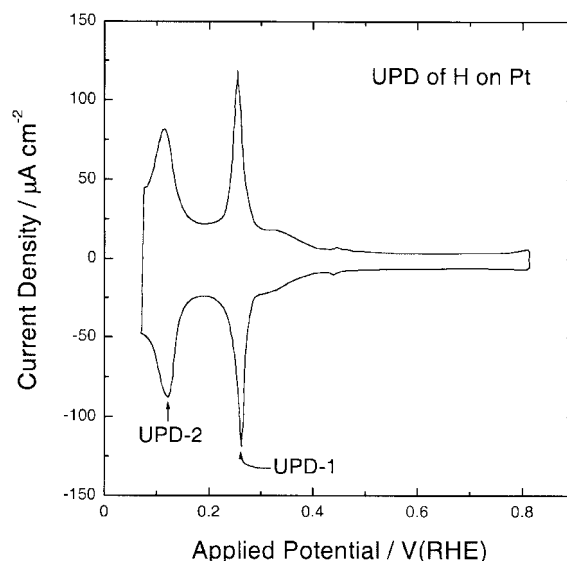
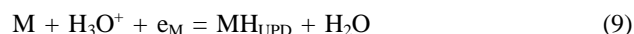


Fig. 2. The cyclic voltammogram measured on the spherical single crystal Pt electrode in 0.5 M H_2SO_4 solution with a scan rate of 50 mV s^{-1} .⁶ The cyclic voltammogram exhibits two current peaks, UPD-1 and UPD-2, corresponding to the underpotential deposition of hydrogen on the Pt electrode.

investigated by employing cyclic voltammetry, giving excellent resolution of the surface processes that are involved. A typical example is presented in Fig. 2. The cyclic voltammogram in Fig. 2 which was taken from the result by Clavilier and Armand,⁶ was obtained from the spherical single crystal Pt electrode in 0.5 M H_2SO_4 solution with a scan rate of 50 mV s^{-1} . As the applied potential moves from 0.8 to 0.07 V(RHE) in the cathodic direction, two current peaks designated as UPD-1 and UPD-2 emerge due to the deposition of hydrogen on the Pt electrode in the potential ranges 0.3 to 0.2 V(RHE) and 0.15 to 0.07 V(RHE), respectively. It should be stressed that these current peaks appear above 0 V(RHE), i.e. at potentials positive to E_{HER} , indicating the UPD of hydrogen. In general, it is well known that a layer of underpotentially deposited hydrogen atoms (H_{UPD}) is formed on such metal surfaces as Pt, Rh, Ir and Pd, prior to the onset of the hydrogen evolution.¹⁹

The UPD of hydrogen on the surface of metal M in aqueous acid solution at potentials above E_{HER} may be represented by the following reaction:



A Langmuir type electrochemical isotherm for this reaction can be written as²²

$$\frac{\theta_{\text{H}_{\text{UPD}}}}{1 - \theta_{\text{H}_{\text{UPD}}}} = a_{\text{H}^+} \exp\left(\frac{-EF}{RT}\right) \exp\left(\frac{-\Delta G_{\text{ads}}^0(\text{H}_{\text{UPD}})}{RT}\right) \quad (10)$$

where $\theta_{\text{H}_{\text{UPD}}}$ is the surface coverage by H_{UPD} ; a_{H^+} , the activity of hydrogen in the solution; E , the applied potential and $\Delta G_{\text{ads}}^0(\text{H}_{\text{UPD}})$ represents the standard Gibbs free energy of adsorption which is a function of $\theta_{\text{H}_{\text{UPD}}}$. In a similar way, the OPD of hydrogen at potentials below E_{HER} and the corre-

sponding electrochemical isotherm may be expressed by the same formulae as reaction (9) and Eq. (10), respectively. However, it is worthwhile noting that the adsorption sites of H_{UPD} and H_{OPD} on the metal surface as well as their standard Gibbs free energies of adsorption $\Delta G_{ads}^0(H)$ can be quite distinguishable.²³⁻²⁹⁾

As a matter of fact, from the studies on the effects of sulphur atoms on the adsorption of hydrogen and the subsequent hydrogen evolution on the Pt electrode, Marcus and Protopopoff²³⁻²⁵⁾ have reported that H_{UPD} and H_{OPD} are distinct species occupying different surface sites, and that the kinetically significant adsorbed species acting as the intermediate in the hydrogen evolution reaction is not H_{UPD} but, rather, H_{OPD} .

Many works³⁰⁻³²⁾ on the UPD and OPD of hydrogen have focussed on the determination of the true adsorption sites of H_{UPD} and H_{OPD} on the metal surface, by employing Fourier transform infrared (FTIR) and other spectroscopies. In those works, the baseline shift observed at the modulation potential above E_{HER} was attributable to the increase in the reflectivity of the metal surface on the adsorption of strongly bound hydrogen corresponding to H_{UPD} . As the modulation potential moved towards and beyond E_{HER} , new absorption bands appeared on the IR spectra, and these bands were assigned to the formation of weakly bound hydrogen corresponding to H_{OPD} .

The experimental results concerning the adsorption sites of H_{UPD} and H_{OPD} can be summarised as follows: H_{UPD} occupies a three-fold hollow site on (111) surface of the face-centered cubic (FCC) and a four-fold one on (100) surface, forming a covalent bond with the substrate metal. On the other hand, H_{OPD} resides on top of the surface metal atom (on-top site), and is bound less strongly to the substrate metal than is H_{UPD} . It has been also recognised that H_{OPD} interacts with H_2O molecules, whereas H_{UPD} does not form a bond with H_2O molecules. The (111) surface of the FCC on which H_{UPD} and H_{OPD} occupy the three-fold site and the on-top site, respectively, is illustrated in Fig. 3. H_{UPD} can be located in two kinds of three-fold hollow sites on the (111) surface of the FCC, i.e. the tetrahedral site and the octahedral site. The theoretical calculation based upon embedded atom method (EAM) indicates that the octahedral site is energetically preferred for H_{UPD} to the tetrahedral one.³³⁾

3.2. Underpotential deposition of hydrogen on Pd and its relation to hydrogen absorption

It has been known that the hydrogen evolution reaction on various transition metals such as Pd, Ti, Zr, and Ni is accompanied by the simultaneous absorption of hydrogen into the metal from a layer of adsorbed hydrogen atoms. For this reason, the role of adsorbed hydrogen in the absorption into such metals has been extensively investigated. Particularly, Pd has been mainly employed in studies designed to explore the absorption of hydrogen, since it exhibits the relatively high hydrogen solubility and diffusivity.³⁴⁾

It is not surprising that H_{OPD} participating in the hydrogen evolution reaction also undergoes the absorption into Pd at potentials below E_{HER} . However, it is not clear whether or

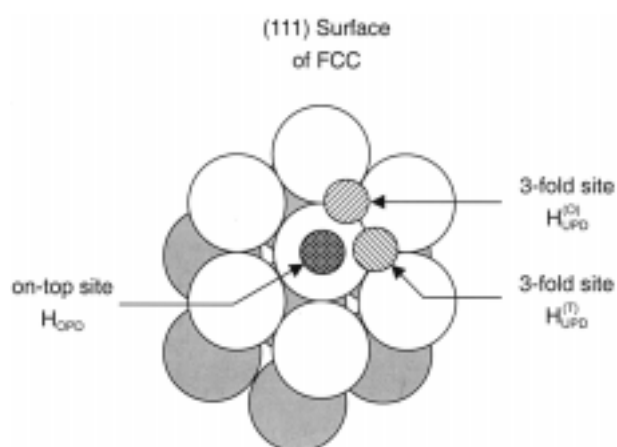


Fig. 3. Schematic diagram of (111) surface of the FCC metals on which the H_{UPD} and H_{OPD} occupy a three-fold hollow surface site and an on-top site, respectively. $H_{UPD}^{(O)}$ and $H_{UPD}^{(T)}$ represent the hydrogen atom in a three-fold octahedral surface site and that atom in a three-fold tetrahedral surface site, respectively.

not H_{UPD} can be absorbed into Pd at potentials above E_{HER} . For the purpose of giving the desired answer to this question, Jerkiewicz and Zolfaghari²⁶⁾ have performed a series of cyclic voltammetric measurements on the Pd electrode in the potential range for the UPD of hydrogen. They have found that when the cathodic potential limit in the cyclic voltammetry was decreased gradually from 0.4 to 0.16 V(RHE), new current peaks markedly different from those peaks due to the UPD of hydrogen emerged below 0.3 V(RHE). They have assigned these new current peaks to the absorption of hydrogen into Pd, and have concluded that the absorption of hydrogen can arise not only from H_{OPD} , but also from H_{UPD} , depending on the applied potential range.

It is readily expected that the absorption mechanism of H_{UPD} into Pd differs from that of H_{OPD} , because of the distinguishable adsorption sites of H_{UPD} and H_{OPD} . On the basis of

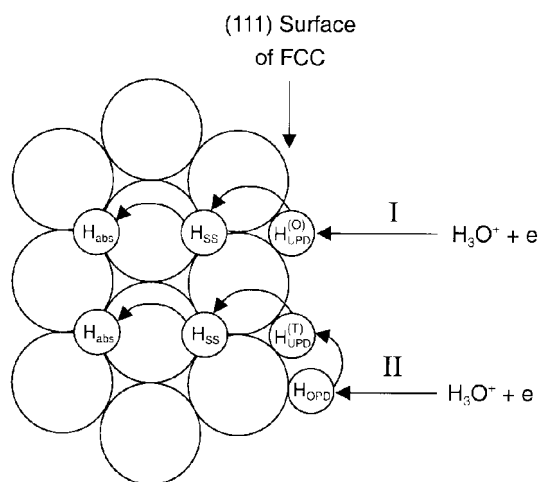


Fig. 4. Schematic view of the mechanism of hydrogen absorption into FCC metals through the (111) surface. H_{SS} is the subsurface hydrogen located between first and second surface layers, and H_{abs} indicates the hydrogen absorbed into an interstice below the second surface layer.

the adsorption sites of H_{UPD} and H_{OPD} discussed in the previous section §3.1, Jerkiewicz and Zolfaghari²⁶⁾ have suggested the atomistic mechanism of hydrogen absorption into FCC metals through the (111) surface, which is visualised in Fig. 4. According to Fig. 4, the first step of the absorption of H_{UPD} occupying a three-fold octahedral surface site involves the interfacial transfer to a subsurface site between two surface layers (H_{SS}). The next step is the absorption into an interstitial site below the second surface layer (H_{abs}), followed by diffusion towards the interior of the bulk metal (mechanism I).

H_{OPD} occupying an on-top site first moves to a three-fold tetrahedral surface site (H_{UPD}), and subsequently undergoes the interfacial transfer and the absorption, by taking the same steps as those in mechanism I (mechanism II). Thus, in this case, H_{UPD} in the three-fold tetrahedral surface site behaves as an intermediate of the absorption process. Considering that the absorption of hydrogen into Pd can take place from H_{UPD} above E_{HER} and from both H_{UPD} and H_{OPD} below E_{HER} , it seems to be reasonable to say that mechanism I can be satisfactorily applied to the absorption process above E_{HER} , while both mechanisms I and II can be effective below E_{HER} .

4. Underpotential Deposition from Practical Viewpoints

UPD is of much greater interest from the practical points of view, since it represents important factors in many areas of electrochemistry including electrocrystallisation, electrocatalysis, corrosion and supercapacitor, some of which are briefly discussed below.

Fundamental aspects of UPD are directly related to electrocrystallisation (electrodeposition) of metals and alloys. The most important parameter determining the mechanism of electrocrystallisation is the binding energy between deposited metal atoms and substrate, provided that the crystallographic misfit between deposited layer and substrate is ignored.^{35,36)} In case that the binding energy between adsorbed metal atoms and substrate is lower than that energy between atoms in the bulk metal of adsorbate, three-dimensional nucleation and growth take place in the OPD range, according to the 'island growth' or 'Volmer-Weber' mechanism.

On the other hand, the sufficiently high binding energy between adsorbed metal atoms and substrate leads to two-dimensional nucleation and growth in the UPD range by the 'layer-by-layer' or 'Frank-Van der Merwe' mechanism. Recently, two-dimensional phase formation based upon UPD process is becoming an accepted method for the formation of thin films for electronic devices in atomic level.³⁵⁻³⁹⁾ As an example, electrochemical atomic layer epitaxy (EC-ALE) for deposition of compound semiconductor thin films such as CdS, InAs and InSb uses the UPD to form atomic layers of each of the component elements.^{37,39)}

Among the interesting aspects of UPD, the most attractive one is its influence on electrocatalysis of organic substances. Especially, the effects of underpotentially deposited metal atoms on the electrocatalytic oxidation of methanol have been widely studied due to its function as a fuel in fuel

cells.⁴⁰⁻⁴²⁾ From the cyclic voltammograms measured on the Pt electrode in alkaline solutions, Beden et al.⁴²⁾ have observed that underpotentially deposited metal atoms such as Pb and Bi enhance the electrocatalytic activity of the Pt electrode on the oxidation of methanol, whereas underpotentially deposited Cd and Tl decrease the oxidation rate of methanol on that electrode. The positive effect of Pb and Bi on the electrocatalytic oxidation of methanol has been explained through the bi-functional theory of electrocatalysis developed by Watanabe and Motoo^{40,41)}, and the negative effect of Cd and Tl has been analysed in terms of the inhibiting behaviour of these metal atoms.

In recent times, the major interest has been manifested in commercial development of electrochemical supercapacitors based upon the UPD of hydrogen or metal atoms that gives rise to large adsorption pseudocapacitance. Conway^{43,44)} has contributed substantially to the understanding of adsorption pseudocapacitance and its application to electrochemical supercapacitors. He has reported that the adsorption pseudocapacitances associated with the UPD of hydrogen on Pt, Rh and Ir are 10-100 times greater than the double-layer capacitances at the same electrodes, giving the possibility of utilising them in high power devices.

5. Concluding Remarks

The present article first explained the fundamentals of UPD, including the concepts of underpotential shift and electrosorption valency. Then, this article presented UPD of hydrogen on metals, giving emphasis to the adsorption sites of hydrogen and the absorption mechanism into Pd. Finally, the present article briefly described the importance of UPD in the fields of electrocrystallisation, electrocatalysis and electrochemical supercapacitors.

UPD is now a well-established phenomenon. A large number of substrate/adsorbate systems exhibiting UPD have been examined by using conventional electrochemical techniques such as cyclic voltammetry to evaluate thermodynamic and kinetic properties of UPD. In the last few years, a renewed interest in UPD has been stimulated by the introduction of scanning tunneling microscopy (STM) to investigate UPD *in-situ*.^{35,36,45)} The STM provides a powerful tool to characterise the structure and morphology of surface layer formed during UPD process. Consequently, the combinations of STM and conventional electrochemical techniques are expected to satisfy the need for understanding UPD in relation to surface phase transition, cluster formation, ordered adsorption and other surface processes.

Acknowledgements

This work was partly supported by the Brain Korea 21 project.

References

1. F. Hilbert, C. Mayer and W. J. Lorenz, *J. Electroanal. Chem.*, **47**,

- 167 (1973).
2. W. J. Lorenz, H. D. Hermann, N. Wüthrich and F. Hilbert, *J. Electrochem. Soc.*, **121**, 1167 (1974).
3. D. M. Kolb, M. Przasnyski and H. Gerischer, *J. Electroanal. Chem.*, **54**, 25 (1974).
4. H. Gerischer, D. M. Kolb and M. Przasnyski, *Surface Science*, **43**, 662 (1974).
5. M. R. Deakin and O. Melroy, *J. Electroanal. Chem.*, **239**, 321 (1988).
6. J. Clavilier and D. Armand, *J. Electroanal. Chem.*, **199**, 187 (1986).
7. E. Lamy-Pitara and J. Barbier, *Applied Catalysis A: General*, **149**, 49 (1997).
8. E. Leiva, *Electrochim. Acta*, **41**, 2185 (1996).
9. W. Schmickler, *Chem. Phys.*, **141**, 95 (1990).
10. S. Trasatti, *Z. Phys. Chem. N. F.*, **98**, 75 (1975).
11. C. Sánchez and E. Leiva, *J. Electroanal. Chem.*, **458**, 183 (1998).
12. J. W. Schultze and K. J. Vetter, *J. Electroanal. Chem.*, **44**, 63 (1973).
13. J. W. Schultze and F. D. Koppitz, *Electrochim. Acta*, **21**, 327 (1976).
14. F. D. Koppitz and J. W. Schultze, *Electrochim. Acta*, **21**, 337 (1976).
15. M. Seo, M. Aomi and K. Yoshida, *Electrochim. Acta*, **39**, 1039 (1994).
16. X. Zeng and S. Bruckenstein, *J. Electrochem. Soc.*, **146**, 2555 (1999).
17. C. Lim and S.-I. Pyun, *Electrochim. Acta*, **38**, 2645 (1993).
18. C. Lim and S.-I. Pyun, *Electrochim. Acta*, **39**, 363 (1994).
19. B. E. Conway and G. Jerkiewicz, *Electrochim. Acta*, **45**, 4075 (2000).
20. A. N. Frumkin and B. Slygin, *Acta Physicochim. URSS*, **3**, 791 (1935).
21. A. N. Frumkin and B. Slygin, *Acta Physicochim. URSS*, **4**, 991 (1936).
22. E. Gileadi, "Electrode Kinetics", 261, VCH Publishers, Inc., New York (1993).
23. P. Marcus and E. Protopopoff, *Surface Science*, **161**, 533 (1985).
24. E. Protopopoff and P. Marcus, *Surface Science*, **169**, L237 (1986).
25. E. Protopopoff and P. Marcus, *J. Vac. Sci. Tech. A*, **5**, 944 (1987).
26. G. Jerkiewicz and A. Zolfaghari, *J. Electrochem. Soc.*, **143**, 1240 (1996).
27. G. Jerkiewicz and A. Zolfaghari, *J. Phys. Chem.*, **100**, 8454 (1996).
28. A. Zolfaghari, F. Villiard, M. Chayer and G. Jerkiewicz, *J. Alloys & Comp.*, **253-254**, 481 (1997).
29. S. Y. Qian, B. E. Conway and G. Jerkiewicz, *Int. J. Hydrogen Energy*, **25**, 539 (2000).
30. A. Bewick and J. W. Russell, *J. Electroanal. Chem.*, **132**, 329 (1982).
31. A. Bewick and J. W. Russell, *J. Electroanal. Chem.*, **142**, 337 (1982).
32. R. J. Nichols and A. Bewick, *J. Electroanal. Chem.*, **243**, 445 (1988).
33. K. Christman, *Surface Science Reports*, **9**, 1 (1988).
34. P. C. Searson, *Acta Metall. Mater.*, **39**, 2519 (1991).
35. W. Obretenov, U. Schmidt, W. J. Lorenz, G. Staikov, E. Budevski, D. Carnal, U. Müller, H. Siegenthaler and E. Schmidt, *J. Electrochem. Soc.*, **140**, 692 (1993).
36. G. Staikov, K. Jüttner, W. J. Lorenz and E. Budevski, *Electrochim. Acta*, **39**, 1019 (1994).
37. L. P. Colletti, D. Teklay and J. L. Stickney, *J. Electroanal. Chem.*, **369**, 145 (1994).
38. E. Budevski, G. Staikov and W. J. Lorenz, *Electrochim. Acta*, **45**, 2559 (2000).
39. T. L. Wade, R. Vaidyanathan, U. Happek and J. L. Stickney, *J. Electroanal. Chem.*, **500**, 322 (2001).
40. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **60**, 259 (1975).
41. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **60**, 267 (1975).
42. B. Beden, F. Kadirgan, C. Lamy and J. M. Leger, *J. Electroanal. Chem.*, **142**, 171 (1982).
43. B. E. Conway, V. Birss and J. Wojtowicz, *J. Power Sources*, **66**, 1 (1997).
44. B. E. Conway, "Electrochemical Supercapacitors", 221, Kluwer Academic / Plenum Publishers, New York (1999).
45. K. Itaya, *Progress in Surface Science*, **58**, 121 (1998).