Vop-Spectroellipsomety and Its Application in Electrochemistry and Solution Chemistry

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1 Introduction

Since the new function Vop was suggested by Huang and Ord in 1983, we have been used the ellipsometry with Vop to study electrochemical reactions for about twenty years. Up to now, we have concluded the new approach "Potential Scanning Ellipsometry"(PSE) for studying electrochemistry qualitatively and the "Electrochemical stripping Ellipsometry"(ESE) for quantitative analysis. Both the PSE and the ESE are reflection optical method getting information from the electrode surfaces. We called them reflection Vop-Spectroellipsometry (Vop-SE).

Recently, we think about a little deficiency of the reflection Vop-SE is that it ask the electrode surface very smooth and absolutely clean, this is not easy for everybody. So that we have tried to explore a new approach for getting information from the solution only. The solution layer for measurement is adjacented to the electrode. Fortunately, we have successfully got a lot of experimental results to characterize the different reactions. Since then, we can analyze a reaction occurred on a electrode or in the solution through the optical parameters Δ, Ψ and their changes during a reaction process. We called this new approach as transmission Vop-SE.

2 Determination of the Vop from the Δ, Ψ measured by ellipsometry

The definition of Vop is:

$$Vop = \sqrt{\frac{x(d\Delta/dt)^2 + y(d\psi/dt)^2}{x+y}} \quad (1)$$

Where $d\Delta/dt$ and $d\psi/dt$ are the variations in Δ and Ψ with time during the reaction processes, the x and y are the weighting coefficients.

We have used the X:y =1:4 for more than eighteen years to determine the Vop empirically, and used the Vop-SE to analyze lots of electrochemical reactions successfully. However, we don't think the empirical proportional constant is accurately enough for any system. For more universal use in any reaction system, we suggest the following definition as the real-time weighting factors of x and y respectively:

$$x = \frac{|d\Delta/dt|}{|d\Delta/dt| + |d\psi/dt|} \quad (2)$$

$$y = \frac{|d\psi/dt|}{|d\Delta/dt| + |d\psi/dt|} \quad (3)$$

Then, after an experiment, one could has a series data of $\Delta_1, \Delta_2, \cdots, \Delta_{i+1}, \cdots \Delta_n$; $\psi_1, \psi_2, \cdots \psi_{i+1}, \cdots \psi_n$; for time $t_1, t_2, \cdots, t_{i+1}, \cdots t_n$. From the $(\Delta_{i+1} - \Delta_i)/(t_{i+1} - t_i)$ and $(\psi_{i+1} - \psi_i)/(t_{i+1} - t_i)$, one could get the $d\Delta/dt$, $d\psi/dt$ and x,y from equation (2) and (3), in company with the definition of Vop, we could have the Vop easily.

3 Summary

This paper concluded the determination of Vop and the application of the new approach Vop-Spectroellipsometry as follows:

(1) The new function Vop can be determine through the optical parameters Δ and Ψ measured directly from the ellipsometry and calculated from the definition of Vop and the related weighting factors x,y.

(2) The reflection Vop-SE can be use to study electrochemical reaction through the variation in Δ and Ψ with time, its sensitivity and accuracy are better than the electrochemical method.

(3) The transmission Vop-SE can be use to study electrochemical reaction, the reaction in solution chemistry or any other liquid system such as the biomedical reaction and so on.

References

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