



Faculty of Engineering

**Simulation and Experimental Validation of Hydrogen Evolution
Reaction using Titanium Carbide Supported, Platinum Doped
Tetrahedral Amorphous Carbon Electrode**

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Simulation and Experimental Validation of Hydrogen Evolution Reaction
Using Titanium Carbide Supported, Platinum Doped Tetrahedral Amorphous
Carbon Electrode

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

This work presented the use of commercial software COMSOL Multiphysics to simulate and solve the Volmer - Heyrovsky –Tafel mechanistic steps for hydrogen evolution reaction (HER). The first study will address the reliability of COMSOL to provide accurate and precise results for electrochemistry problem. The developed model is for classical cyclic voltammetry of redox reaction (E). In this study, mesh refinement with its consequent number of elements (noe), computation time (t_{com}), and current, $I(t)$ was compared on the 1-dimension (1D), 2-dimension (2D) axisymmetric, and 3-dimension (3D) model. This study proved the software's consistency to produce less than 3% error between simulation and analytical results across all dimensions. By using a relative tolerance ($rtol$) value of 1×10^{-8} with very concentrated custom meshing, a 3D model yielded a result with an error of 2.5% compared to analytical solution. It has the drawback of taking 40 times longer to complete. A slight discrepancy between 2D axisymmetric and 3D simulation results on finest meshing recorded to have less than 3% difference due to CPU memory limit. The use of adaptive meshing on 2D axisymmetric and 3D model with coarse initial mesh reduces the error significantly by 32% and 50%, respectively. At the same time, the computation time, t_{com} increased by nearly ten times on the 2D axisymmetric model and five times on the 3D model. On the “finer” initial mesh, the simulation has reduced the error to near 0%. The $rtol$ study shows that the value of 1×10^{-4} is adequate for 2D axisymmetric and 1×10^{-5} for both 1D and 3D. Further investigations on complex electrochemistry using this platform are well justified and highly recommended. Given the reliability of COMSOL presented in the first study, the second study implement similar approach to model the experiment by Glandut et. al (2015) on Titanium carbide (TiC) support, tetrahedral amorphous carbon doped platinum (taC:Pt) electrode for hydrogen evolution reaction. The developed model was tested for surface

diffusion in 2D and surface diffusion with edge effect in 3D. The simulation results show that kinetic parameters permutation with surface diffusivity shows some increased in current output but was unable to achieve the current output obtained from the experiment. However, the introduction of edge effect on the side of taC:Pt on TiC support would significantly increase the current output with great coherency to the experimental result. The edge exhibits kinetic properties unlike both TiC or taC:Pt. The kinetic parameters were determined using the simulation and a dataset was found to show great coherency with the experimental result. Surface diffusion was rendered negligible because negligible compared to the high kinetic parameters on the edge in comparison to the TiC and taC:Pt surface.

Keywords: Simulation, COMSOL, redox reaction, mesh refinement, hydrogen evolution reaction (HER), surface diffusion, edge effect

Simulasi dan Pengesahan Eksperimen Tindak Balas Evolusi Hidrogen Menggunakan Titanium Carbide Disokong, Elektrod Karbon Amorfus Tetrahedral Doped Platinum

ABSTRAK

Kerja ini membentangkan penggunaan perisian komersial COMSOL Multiphysics untuk mensimulasikan dan menyelesaikan langkah mekanistik Volmer - Heyrovsky -Tafel untuk tindak balas evolusi hidrogen (HER). Kajian pertama akan menangani kebolehpercayaan COMSOL untuk memberikan keputusan yang jitu dan tepat untuk menyelesaikan masalah elektrokimia. Model yang dibangunkan adalah untuk voltammetri kitaran. Dalam kajian ini, penghalusan jejaring dengan bilangan unsur (noe), masa pengiraan (t_{com}), dan arus, $I(t)$ telah dibandingkan pada paksisimetrik 1-dimensi (1D), 2-dimensi (2D), dan 3 -model dimensi (3D). Kertas kerja ini membuktikan ketekalan perisian untuk menghasilkan ralat kurang daripada 3% antara simulasi dan keputusan analisis merentas semua dimensi. Dengan menggunakan nilai toleransi relatif ($rtol$) 1×10^{-8} dengan jejaring tersuai yang sangat padat, model 3D menghasilkan keputusan dengan ralat 2.5%. Ia mempunyai kelemahan iaitu mengambil masa 40 kali lebih lama untuk disiapkan. Sedikit percanggahan antara paksisimetri 2D dan simulasi 3D menghasilkan jalinan terbaik yang direkodkan mempunyai perbezaan kurang daripada 3% disebabkan oleh had memori CPU. Penggunaan jejaring adaptif pada model axisymmetric 2D dan 3D dengan jejaring awal kasar mengurangkan ralat dengan ketara masing-masing sebanyak 32% dan 50%. Pada masa yang sama, t_{com} meningkat hampir sepuluh kali ganda pada model axisymmetric 2D dan lima kali pada model 3D. Pada jaringan awal yang "lebih halus", simulasi telah mengurangkan ralat kepada hampir 0%. Kajian $rtol$ menunjukkan bahawa nilai 1×10^{-4} adalah memadai untuk axisymmetric 2D dan 1×10^{-5} untuk kedua-dua 1D dan 3D. Siasatan lanjut mengenai elektrokimia kompleks menggunakan platform ini adalah wajar dan sangat

disyorkan. Memandangkan kebolehpercayaan COMSOL yang dibentangkan dalam kajian pertama, kajian kedua melaksanakan aplikasi yang hampir serupa untuk memodelkan eksperimen oleh Glandut et. al (2015) mengenai sokongan Titanium karbida (TiC), elektrod platinum dop karbon amorfus tetrahedral (taC:Pt) untuk tindak balas evolusi hidrogen. Model yang dibangunkan telah diuji untuk resapan permukaan dalam 2D dan resapan permukaan dengan kesan tepi dalam 3D. Keputusan simulasi menunjukkan bahawa pilihatur parameter kinetik dengan keresapan permukaan menunjukkan beberapa peningkatan dalam arus litar tetapi tidak dapat mencapai arus yang diperolehi daripada eksperimen. Walau bagaimanapun, pengenalan kesan tepi pada sisi taC:Pt pada sokongan TiC akan meningkatkan arus litar dengan ketara dengan keselarasan yang besar kepada hasil eksperimen. Tepi mempamerkan sifat kinetik tidak seperti kedua-dua TiC atau taC:Pt. Parameter kinetik ditentukan menggunakan simulasi dan set data didapati menunjukkan keselarasan yang besar dengan keputusan eksperimen. Penyebaran permukaan tidak berguna kerana parameter kinetik yang sangat tinggi di tepi berbanding dengan permukaan TiC dan taC: Pt.

Kata kunci: *Simulasi, COMSOL, reaksi redox, penghalusan jejaring, reaksi evolusi hidrogen, keresapan permukaan, kesan tepi*

Simulation et validation expérimentale de la réaction d'évolution de l'hydrogène à l'aide d'une électrode de carbone amorphe tétraédrique supportée par du carbure de titane et dopée au platine

RÉSUMÉ

Ce travail a présenté l'utilisation du logiciel commercial COMSOL Multiphysics pour simuler et résoudre les étapes mécanistes Volmer - Heyrovsky –Tafel pour la réaction d'évolution de l'hydrogène (HER). La première étude portera sur la fiabilité de COMSOL à fournir des résultats exacts et précis pour un problème d'électrochimie. Le modèle développé est pour la voltamétrie cyclique sous diffusion sphérique semi-infinie. Dans cette étude, le raffinement du maillage avec son nombre conséquent d'éléments (noe), son temps de calcul (t_{com}) et son courant, $I_{(t)}$ a été comparé sur la 1 dimension (1D), la 2 dimension (2D) axisymétrique et la 3 modèle tridimensionnel (3D). Cet article a prouvé la cohérence du logiciel pour produire moins de 3% d'erreur entre la simulation et les résultats analytiques dans toutes les dimensions. En utilisant une valeur de tolérance relative (rtol) de 1×10^{-8} avec un maillage personnalisé très concentré, un modèle 3D a donné un résultat avec une erreur de 2,5 %. Il a l'inconvénient de prendre 40 fois plus de temps à compléter. Un léger écart entre les résultats de simulation 2D axisymétrique et 3D sur le maillage le plus fin enregistré a moins de 3 % de différence en raison de la limite de mémoire CPU. L'utilisation du maillage adaptatif sur le modèle 2D axisymétrique et 3D avec un maillage initial grossier réduit l'erreur de manière significative de 32 % et 50 %, respectivement. Dans le même temps, le t_{com} a été multiplié par près de dix sur le modèle axisymétrique 2D et par cinq sur le modèle 3D. Sur le maillage initial "plus fin", la simulation a réduit l'erreur à près de 0%. L'étude rtol montre que la valeur de 1×10^{-4} est adéquate pour le 2D axisymétrique et 1×10^{-5} pour le 1D et le 3D. D'autres investigations sur l'électrochimie complexe utilisant cette plate-forme sont bien justifiées et fortement recommandées. Compte tenu de la fiabilité de

COMSOL présentée dans la première étude, la seconde étude met en œuvre une application quasi similaire pour modéliser l'expérience de Glandut et. al (2015) sur support en carbure de titane (TiC), électrode en platine dopé au carbone amorphe tétraédrique (taC:Pt) pour la réaction de dégagement d'hydrogène. Le modèle développé a été testé pour la diffusion de surface en 2D et la diffusion de surface avec effet de bord en 3D. Les résultats de la simulation montrent que la permutation des paramètres cinétiques avec la diffusivité de surface montre une certaine augmentation de la sortie de courant mais n'a pas été en mesure d'atteindre la sortie de courant obtenue à partir de l'expérience. Cependant, l'introduction d'un effet de bord du côté de taC:Pt sur le support TiC augmenterait considérablement la sortie de courant avec une grande cohérence avec le résultat expérimental. Le bord présente des propriétés cinétiques contrairement à TiC ou taC:Pt. Les paramètres cinétiques ont été déterminés à l'aide de la simulation et un ensemble de données a été trouvé pour montrer une grande cohérence avec le résultat expérimental. La diffusion de surface a été rendue inutile en raison des paramètres cinétiques extrêmement élevés sur le bord par rapport à la surface TiC et taC:Pt.

Mots clés: *Simulation, COMSOL, réaction redox, raffinement de maillage, réaction de dégagement d'hydrogène (HER), diffusion de surface, effet de bord.*

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