

**ELECTRODE FOR IMPROVING ELECTROCHEMICAL
MEASUREMENTS IN HIGH TEMPERATURE WATER**

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ABSTRACT

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Potentiometric measurements in high-temperature water/platinum
electrode

A silver/silver-chloride (Ag/AgCl) reference electrode was specially designed and constructed in a body of oxidized titanium for potentiometric measurements under high-temperature and high-pressure conditions. To avoid the thermal decomposition of silver-chloride, the electrode was designed to maintain the reference element at low temperature while it is connected to a high-temperature process zone via a non-isothermal electrolyte bridge. This configuration leads to the development of a thermal gradient along the length of the electrode. At room temperature, the stability of the Ag/AgCl reference electrode versus a standard calomel electrode (SCE) was maintained with an accuracy of ± 5 mV. The performance of the electrode at high temperature and pressure (up to 300 °C and 1500 psi) was examined by measuring the potential difference against platinum, which acted as a reversible hydrogen electrode (RHE). A comparison of the experimental and theoretical values verified the reliability and reproducibility of the electrode. Deviation from the Nernst equation was considered and related to the liquid junction potential (LJP), the thermal liquid junction potential (TLJP) and the titanium oxide reaction potential (E_{TiO_2}). An empirical correction factor is used to convert the measured potential against the Ag/AgCl reference electrode onto a standard hydrogen electrode (SHE) scale within an accuracy of ± 17 mV at high temperature.

บทคัดย่อ

ฐานิยี่ เซ่งอาศัย: อีเล็ทโทรดสำหรัการพัฒนาการวัดโพเทนเชีลในน้ำอุณหภูมิสูง (Electrode for Improving Electrochemical Measurements in High Temperature Water) อ. ที่ปริกษา: รศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ, ผศ.ดร. วิลเลียม คุก และ ศ. แฟรงค์ อาร์ สจิวัด 61 หน้า ISBN 974-9937-37-6

ได้ออกแบบและสร้างอีเล็ทโทรดครึ่งเซลล์มาตรฐานอ้างอิงซิลเวอร์/ซิลเวอร์คลอไรด์ เป็นพิเศษด้วยวัสดุประเภทไททานเนียมออกไซด์สำหรัการวัดค่าความต่างศักย์ของเซลล์ใดๆ ภายใต้อุณหภูมิและความดันสูง อีเล็ทโทรดได้รับการออกแบบเพื่อหลีกเลี่ยงการละลายของซิลเวอร์คลอไรด์จากความร้อนและยังคงเชื่อมต่อกับบริเวณอุณหภูมิสูงผ่านทางสะพานอีเล็ทโทรไลต์ ที่อุณหภูมิไม่คงที่ซึ่งส่งผลให้เกิดความแตกต่างของอุณหภูมิของสารละลายภายในอีเล็ทโทรด จากการศึกษาที่อุณหภูมิห้องพบว่า ความต่างศักย์ของอีเล็ทโทรดครึ่งเซลล์มาตรฐานอ้างอิงซิลเวอร์/ซิลเวอร์คลอไรด์เทียบกับอีเล็ทโทรดมาตรฐานคาโลเมลมีความเสถียรภายใน 5 มิลลิโวลต์ ความสามารถในการทำงานของอีเล็ทโทรดที่อุณหภูมิและความดันสูง (300 องศาเซลเซียส และ 1500 ปอนด์/นิ้ว²) หาได้จากการวัดความต่างศักย์เทียบกับอีเล็ทโทรดครึ่งเซลล์แพลตตินัมซึ่งทำหน้าที่แทนอีเล็ทโทรดครึ่งเซลล์มาตรฐานไฮโดรเจนแบบผันกลับได้ เมื่อเปรียบเทียบค่าจากการทดลองกับค่าที่คำนวณได้ทางทฤษฎีพบว่าค่าเบี่ยงเบนจากสมการเนิร์สเกิดจากค่าความต่างศักย์ ณ จุดรอยต่อของสารละลาย ค่าความต่างศักย์ที่เกิดจากความแตกต่างของอุณหภูมิภายในอีเล็ทโทรด และค่าความต่างศักย์ของปฏิกิริยาไทเทเนียมไดออกไซด์ ค่าเบี่ยงเบนดังกล่าวถูกนำมาใช้ในการสร้างสมการทางคณิตศาสตร์เพื่อเปลี่ยนค่าความต่างศักย์วัดเทียบกับอีเล็ทโทรดครึ่งเซลล์มาตรฐานอ้างอิงซิลเวอร์/ซิลเวอร์คลอไรด์เทียบกับอีเล็ทโทรดครึ่งเซลล์ไฮโดรเจนมาตรฐาน โดยมีค่าความถูกต้องภายใน 17 มิลลิโวลต์ภายใต้การทำงานที่อุณหภูมิสูง

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ABBREVIATIONS

BWR	Boiling water reactor
CE	Counter electrode
ECP	Electrochemical corrosion potential
EPBRE	External pressure balanced reference electrode
IGSCC	Inter granular stress corrosion cracking
FTEPBRE	Flow through external pressure balanced reference electrode
IRE	Internal reference electrode
LJP	Liquid junction potential
LWR	Light water reactor
NHE	Normal hydrogen electrode
RE	Reference electrode
RHE	Reversible hydrogen reaction
SCC	Stress-corrosion cracking
SCE	Standard calomel electrode
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
TLJP	Thermal liquid junction potential
WE	Working electrode
XRD	X-ray diffraction
YSZ	Yttrium-stabilized zirconia

LIST OF SYMBOLS

a_{Cl}	chloride ion activity
a_{H^+}	hydronium ion activity
a_i^L	activity of species on the left hand side of the boundary region
a_i^R	activity of species on the right hand side of the boundary region
A_0	the first regression coefficient for thermal liquid junction potential calculation
A_1	the second regression coefficient for thermal liquid junction potential calculation
A_2	the third regression coefficient for thermal liquid junction potential calculation
A_3	the fourth regression coefficient for thermal liquid junction potential calculation
E_{AgCl}	silver/silver-chloride electrode potential at given temperature
E_{AgCl}^o	the standard silver/silver-chloride electrode potential
E_{H^+/H_2}	potential of the hydrogen reaction on platinum electrode at given temperature
E_{H^+/H_2}^o	The standard potential of the hydrogen reaction on platinum electrode
E_{Pt}	platinum electrode potential
E_{TiO_2}	the titanium dioxide reaction potential
E_r	reversible potential difference at metal/solution interface
E^*	potential deviation
ΔE_{meas}	measured potential difference
ΔE_{SHE}	potential of electrode of interest on SHE scale
G^o	standard free energy of formation
ΔG_r	reaction free energy

K_w	dissociation equilibrium constant of water
n	number of electron transferred
P_{H_2}	partial pressure of hydrogen gas
R	gas constant
S^*	entropy of transport
t	transport number
u	ion mobility
ΔT	T-298.5 K
z	ion charge
γ_{Cl}	chloride ion activity coefficient
δ	average compensating term for parallel electrolyte conduction paths