PLATINUM ELECTROCHEMISTRY (EIS DATA) & CORROSION MECHANISM UNDER ASSYMMETRIC PULSES STIMULATION

Aleksandr PIKELNY
and
Darryl HWANG

Alfred Mann Foundation
28460 Avenue Stanford, Valencia, CA 91355
E-mails: alagpik@worldnet.att.net
dhwang@aemf.org

INTRODUCTION

As was described previously [1-3], platinum electrodes can be undergoes degradation under consistent pulses polarization. Despite three decades of investigation, there are no clear power limits for their applications. Usually as criterion for these limits many authors use co-called charge injection density or charge per phase [2, 3].

Reported “safe” limits very often differ by orders of magnitude and contain qualitative rather than quantitative information. The influences of solution composition, aeration, operational mode (anodic first – cathodic first) and temperature are not clear.

Our goal was, by using EIS technique, to investigate electrochemical behavior of platinum with correlation to proposed corrosion mechanism.

RESULTS and DISCUSSION

The implantable microstimulator [4] has two electrodes (stimulus and indifferent) and produces asymmetric capacitively coupled electrical pulses. These electrodes have “mirror” polarization and red-ox behavior during unit’s operation. Despite cathodic polarization, stimulus electrode has higher average potential, and is more affected by the corrosion process than indifferent. Corrosion measurements show high data deviation [1]. Process also correlated with the overall potential and potential scan during the stimulation.

EIS data as a Bode plot show that platinum in potential interval from 0 to 0.4 V (Ag/AgCl) behaves as an ideal capacitor, for which the slope of the Log Z vs. Log f plot is –1, and Φ value close to 90°. At higher potentials a second well-defined flat region on Z-frequency plot and maximum on phase angle-frequency appear.

The Nyquist plots are shown on figure. At potentials below 0.4 V, when platinum electrode demonstrates capacitance behavior, impedance is high, which is typical for stable films. As potential increased, lower values of impedance indicate enhanced dissolution. In the potential region from 0.6 to 0.8 V impedance drops more than two orders of magnitude.

On the basis, that behavior of noble metals can be strongly influenced by the conditions of their surface [5] and depends on solution environment [6], proposed corrosion mechanism includes.

Processes on platinum under negative potential shift:

Double layer charge (discharge).
Platinum oxides reduction.
Hydrogen adsorption.
Hydrogen penetration in the bulk of metal.

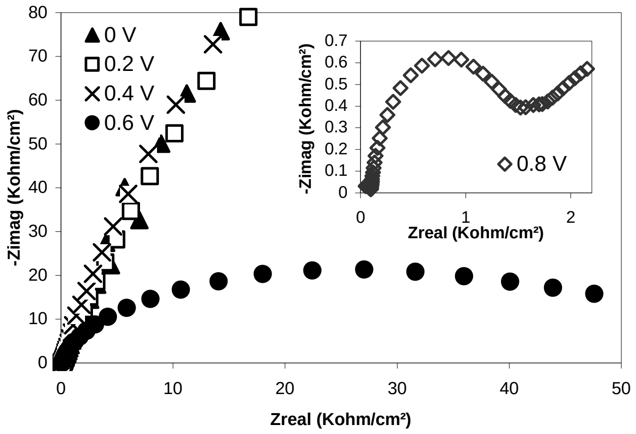
Processes, which take place during positive potential shift:

Double layer charge (discharge).
Adsorbed hydrogen desorption.
Platinum oxides formation.
Place exchanging mechanism of oxygen and platinum atoms [7].

If the initial potential of platinum is more positive, the amount of platinum oxides formed during potential shift in the positive direction increases in comparison with the situation when the positive impulse of current starts in platinum “hydrogen” area.

Depending on the amount of formed platinum oxides and the negative pulse amplitude and duration, not all of the oxides can be reduced. This phenomenon is especially true for platinum oxides (or absorbed oxygen) in the bulk of metal, formed due to the place exchanging mechanism [7]. Even if the surface of platinum is oxides-free, it is possible for oxygen to be present in the bulk of metal.

Formed hydrogen diffuses in the bulk of metal and reacts with the absorbed oxygen, which results in metal degradation.



Nyquist plots of platinum in PBS at 37°C and different potentials (Ag/AgCl): (▲) – 0 V; (□) – 0.2 V; (x) – 0.4 V; (✱) – 0.6 V; (◊) – 0.8 V (insert).

On the basis of the proposed corrosion mechanism vast experimental data of platinum corrosion is explained.

REFERENCES

1. A. Pikelny, P. Mobley and J. Schulman, in *Meeting Abstracts*, PV 2002-2, Abstract No. 358, The Electrochemical Society, Salt Lake City, UT (2002).
2. S. B. Brummer, J. McHardy and M. J. Turner, in *Brain, Behavior and Evolution*, No 14*:* p. 10, New York, (1977).
3. D. B. McCreery, W. F. Agnew, T. G. H. Yuen and L. Billara, in *IFESS Journal of Biomedical Engineering*, No 10, (1990).
4. A. Dupont, S. D Bagg, J. L. Creasy, C. Romano, G. E. Loeb and F. J. R. Richmond, in *IFESS 2001 Processing*, p.7, Cleveland, Ohio (2001).
5. J. O’M. Bockris and A. K. N. Reddy, in *Modern Electrochemistry*, Plenum Press, NY (1970).
6. J. Van Muylder, N. de Zoubov, and M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions by Marcel Pourbaix*, Section 13.6, p. 378, National Association of Corrosion Engineers (1977).
7. H. You, Z. Nagy, D. J. Zurawski and R. P. Chiarello, in *Electrochemical Society Proceeding Volume* 96-8, p. 136, The Electrochemical Society, Pennington, NJ (1968).