

**Electrochemical Impedance Spectroscopy
Measurements of the Passivation of Dimensionally
Stable Anodes**

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Titanium-based substrates with coatings containing ruthenium dioxide or iridium dioxide are the standard anodes for generating chlorine in the chlor-alkali, chlorate and hypochlorite industries. While these Dimensionally Stable Anodes (DSA[®]) have very long lifetimes, they ultimately experience voltage escalations due to the growth of a high resistance layer of titanium oxide between the active coating and the substrate. This growth can be triggered not only by length of service but also by upsets in the electrolysis conditions (e.g. deposits from contaminants). Detection of the passivation layer is key to understanding the state of the anode and whether the performance can be restored. However, since the resistance of titanium (sub)oxide can vary by upwards of 12 orders of magnitude, only very thin layers are required to cause the anode potential to increase significantly. Detection of this thin oxide layer usually requires destructive techniques (e.g. cross-sections with SEM) but locating the layer is actually very problematical during the early growth period. However, a non-destructive Electrochemical Impedance Spectroscopy (EIS) technique can be utilized to examine the anode and determine whether or not a passivation layer is present¹. The technique is capable of distinguishing between increases in potential due to surface deposits or the passivation layer.

By attaching a computer controlled EIS system to a laboratory, accelerated lifetest system, the progress of the growth of the passivation layer can be followed *in situ* with periodic measurements (Fig. 1). The phase angle is correlated to the change in cell voltage (anode potential) with time (Fig. 2). The EIS data generated over the lifetime of the anode can be fitted to an equivalent circuit such as in Figure 3. The change in the fit parameters can be correlated with the change in anode potential with time. Preparation of various types of samples has demonstrated that the EIS parameters can be associated with regions that are predominately due to the active coating or the result of the growth of the titanium oxide layer.

Samples from commercially operated chlor-alkali or chlorate anodes have been examined using the EIS technique. The high voltages associated with some of these anodes have been shown by the EIS technique to be the result of the onset of passivation. In other cases there is no indication of passivation, indicating that the high voltages are likely the result of surface deposits, which were subsequently identified. This data is useful in establishing whether anodes should be just cleaned or whether recoating is necessary.

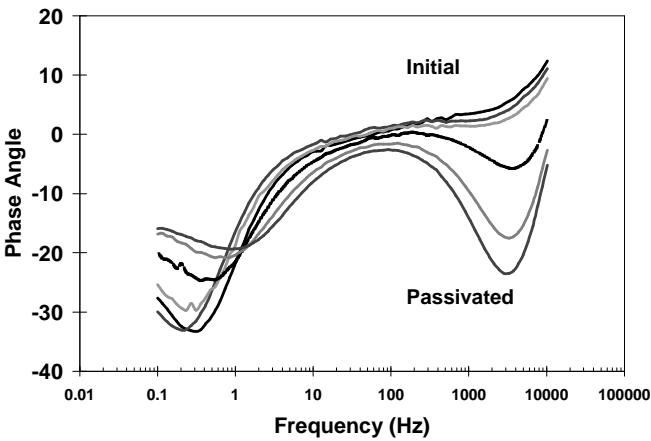


Figure 1: Sequence of EIS Curves as a Function of Time for a RuO₂/IrO₂ Coating on Titanium.

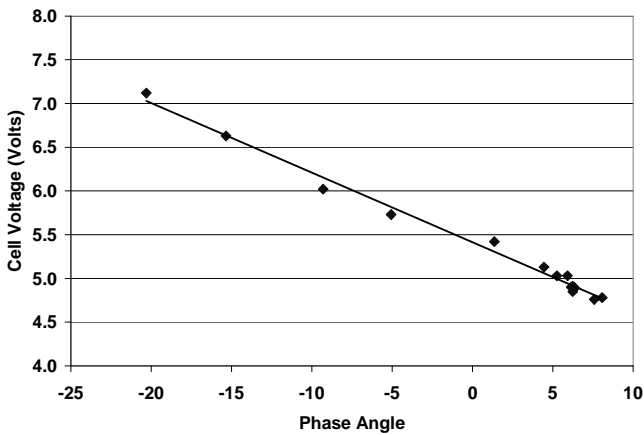


Figure 2: Correlation of Cell Voltage with Change in Phase Angle from EIS Data in Figure 1

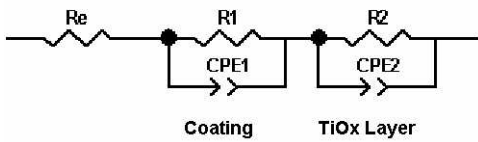


Figure 3: Equivalent Circuit for Fitting EIS Data for a Passivated Titanium Anode

References:

¹ K.L. Hardee and R.A. Kus, Modern Chlor-Alkali Technology, S. Sealey, ed., Vol. 7, p.43-54, 1998

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