

JBCE answer for questions by email on the 22nd January 2013

Exemption Request 13 “Lead in platinized platinum electrodes for measurement instruments”

1. Add a road plan for research of substitutes (substances) or alternatives (technologies) for the use of lead in the application.
 - a. What directions may be relevant for future research?

There would be the following three directions for future research.

- 1) Substitute of substance (no lead) or decreasing use of lead (less than 0.1 %) for platinised platinum electrode
- 2) Substitute of material for electrode
- 3) Alternative of measurement method

- b. Do you know of any relevant research that is already on-going?

- 1) We have not found any further research and development after the report of Feltham, A. M. and Spiro M., “Platinized Platinum Electrode”, Chemical Reviews, 1971, Vol. 71No. 2, pp 177 – 193.
- 2) As is seen in the Table 1 we provided before , the substitution of the material for electrode has been realized, so far as the high specification (for example, wide range measurement, high accuracy, high reliability under extreme acidic/alkaline condition, or small size) is not required. For the high specification, however, appropriate alternatives have not found yet.
- 3) Similarly to 2) appropriate methods have not found yet for the high specification

- c. Once a substitute or alternative is found, how much time will be needed for the various stages before RoHS compliant applications can come on the market
 - minimal needed time for research into substitutes or alternatives
 - time needed for product redesign
 - time needed for reliability testing
 - time needed for product approval according to standards or regulations if such apply

- minimal needed time for research into substitutes or alternatives

This is the most important stage after a candidate substitute or alternative is found. At first we have to test the substitutes on the component level. And then we have to confirm the performance by using theoretical calculation/simulation software. It takes 1 – 2 years.

- time needed for product redesign

It takes 1 – 2 years to redesign one product: finalising product specification, making proto-type, verifying it, and designing for mass-production. For redesigning various types of the products we need 3 – 4 years.

This is the minimum time we need for the case when we obtain the substitutes or alternatives of very good quality: time for redesign depends on the quality level of substitute or alternative.

- time needed for reliability testing

Including field test, it takes 1 – 2 years.

- time needed for product approval according to standards or regulations if such apply

If any substitutes or alternatives should be used, the standard should be amended, because the current standard (EN27888:1993 which is equivalent to ISO7888:1985) is based on the platinised platinum electrodes. We do not know how fast the standard will be amended and how much influence may arise back to product redesign work.

In a summary mentioned above at least 2 – 4 years as total are needed per one product. For the various products 4– 6 years are needed. If we cannot carry out reliability test at the early stage of redesign process in parallel, we need additional 1– 2 years. In addition, we would like to emphasize that in practice a full model change for the electrodes of high quality takes place in a 7–year cycle or longer. To shorten the cycle means that manufacturers need extra manpower, or have to sacrifice other equipment planned to develop.

2. What is determines the relation between surface area of the electrode and size (dimensions)?

Resistivity is equivalent to electrical resistance per unit area and unit length. The resistance between two electrodes R (Ω) is

$$R = \rho_0 (L/A) \text{ ----- (1)}$$

Where ρ_0 is the electrical resistivity, A (m^2) is the area, and L (m) is the length.

Therefore, the electric conductivity K_0 (S/m) is

$$K_0 = 1/\rho_0 = (1/R) (L/A) \text{ ----- (2)}$$

When L/A is known, K_0 can be obtained by measuring R (Ω) between electrodes.

The cell constant $C1$ ($/m$) is given as equation (3):

$$C1 = L1/A1 (/m) \text{ ----- (3)}$$

Where $A1$ (m^2) is the Surface area of electrode and $L1$ (m) is the distance between electrodes.

Therefore, the electric conductivity K_0 (S/m) is given as equation (4):

$$K_0 = (1/R) C1 \text{ ----- (4)}$$

The polarisation impedance of capacitance at the surface boundary between electrode and solution is $1/(2\pi fC)$. Measurement error occurs, when the polarization impedance is added to the resistance of the solution.

For the accurate measurements, $2\pi fC$ should be large. In order to obtain the large $2\pi fC$, both the accelerated frequency and the capacitance created between electrodes should be high. This can be achieved either by platinised platinum that can enlarge surface area of electrode for solution to approximately 1000 times of flat electrode or by sizing up surface area of electrode itself. For example, if f is 1 [kHz] and C is [10,000 μF], the polarisation impedance is equal to $1/(2 \times 3.14 \times 1000 \times 10^{-2}) =$ approximately 0.02Ω and the error is negligible.

Therefore, if the platinised platinum is not used, surface area of electrode itself has to be larger.

(Please refer to (b) in original application.)

3. Consequently, if platinization was not preformed;
- a. What would be the parallel size of the electrodes (if there are various sized models, give a few examples).

As is shown in Table 2-1, the capacitance and polarization impedance are different between the case with lead and without lead. Figure 1 (The data from Table 2-2) indicates that for the platinum with lead $L=1.00[\text{cm}]$, $A=1.00[\text{cm}^2]$ is enough to get approximately 0.35 % error, while a set of electrodes of $L=500[\text{cm}]$, $A=500[\text{cm}^2]$ is needed for platinum without lead or for titanium plate.

Thus, it is not possible to measure the conductivity of a small amount of solution with platinum plate without lead or titanium plate. The large size is, moreover, against resource saving, as well as against eco-design.

- b. Would this require additional changes to the final product (i.e., change in energy consumption, change in application size, change in amount of platinum needed for manufacturing the electrode) please detail the estimated magnitude of possible needed alterations.
 - 1) If the size of the electrodes becomes larger, the size of the final products becomes larger, that hinders measurements in many cases.
 - 2) The range of the measurable conductivity narrows. Therefore, several different electrodes are needed to perform one measurement. For example, in the case of a process control, the electric conductivity of the process solution is monitored on-line. If the measurement range is from 50 [mS/m] to 5 [S/m], two electric conductivity electrodes (AC2, cell constant: 5000/m and AC4, cell constant: 1000/m) and the two corresponding meters have to be installed. (Please refer the reference material provided previously, and also table1 and figure 1 provided with this answer.) In the case of measurement in laboratory for research purpose, they always need to have several types of electrodes under the stand-by condition. If they use the electrode of electromagnetic induction type, much more sample (solution) is needed: the difference of the amount is beakerful and a bucketful.

As a conclusion many of the measurements will be hindered because of lack of the space and because of the increase of the cost. Since the conductivity measurements are essential for environment, as well as product quality, negative impact is very strong if only the current available substitutes/alternatives are used.

