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The Use of the Vibrating Electrode Method for Surface and Bulk Characterization of Solid Samples

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In order to investigate the potential existing at solid — air interface of solid samples an apparatus has been designed. The sample cell does not contain any chemical referent electrode. The influence of the cell itself on the measured potential can be eliminated by blank potential measurements of the sample support surface. The design allows to apply a known potential difference to the sample surface so that the sensitivity and accuracy of the measurement can be precisely determined.

Methods for measuring conducting and nonconducting samples were developed. The equations analyzing the experimentally obtained potentials for all the studied cases were presented.

Special attention was paid when dealing with nonconducting samples having a bulk polarization. It was shown that bulk polarization influenced the result obtained by vibrating electrode procedure. A method for the determination of this additional potential component is proposed.

INTRODUCTION

The vibrating electrode method as a tool for measuring the Volta potential existing at an interface is an old method based on Kelvin's experiments in 1898[1] and Zisman's modifications[2,3]. Since its origin the method has been improved and modified by many authors. The review of articles concerning this method can be found in ref. 4. This method has been mainly used for potential difference analyses at liquid-gas interfaces. Only in a few cases the vibrating electrode method has been applied for the investigation of other systems, such as: liquid-liquid[5], solid-liquid[6] and solid-gas[7] interfaces.

The aim of this paper is to examine the experimental and theoretical possibilities of measuring the contact potential at solid-gas interfaces using various types of solid samples: electric conductors and insulators.

EXPERIMENTAL

A schematic block diagram of the apparatus used is shown in Fig. 1. The assembly was designed without reference electrode. The compensation voltage was not applied at the sample, but at the vibrating electrode. For the generation of the mechanic oscilations a small loudspeaker (25 Ω/1W) was used. For driving the electrode an energy as small as 0.2 W was sufficient. The signal generated on the vibrating electrode was led to the input stage of the preamplifier PPA. This first stage of amplification contained n-channel FET, 2n 4416 transistor located inside the sample cell. The output of the transistor was connected to an external pre-

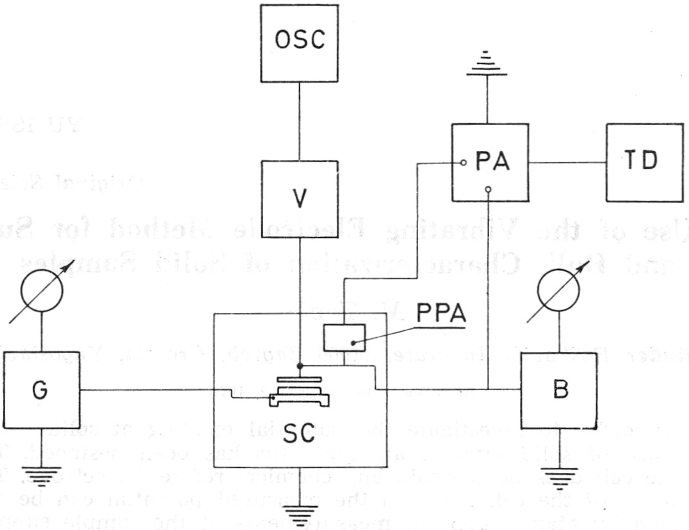

Fig. 1 — Block schematic diagram. G — potential divider for supplying the sample support; B — potential divider, the source of bucking voltage; SC — sample cell; OSC — RC oscilator, 200 Hz; V — mechanic vibrator; PPA — input stage of preamplifier; PA — preamplifier; TD — 1232 — A General Radio tuned amplifier and detector

amplifier PA by coaxil cables. The PPA and PA were built as described in ref. 7. The determination of the contact potential U_t existing at a sample-air interface was carried out by a bucking voltage U_b generated in B and applied to the vibrating electrode. In the case when $U_b = U_t$ there is no current passing through the air gap between sample and electrode and no signal will be observed by detector TD. In order to check the accuracy of the measurements it is possible to simulate a known potential difference at the sample-air interface. For that purpose the potential divider G was used, and generated potential U_g was applied directly to the sample support.

The sample cell and vibrator can be seen in detail in Fig. 2. The vibration transmitter T made from ceramic tube is attached directly to the center of the vibrating loudspeaker membrane. By using connector M, ring MR and one or more thin sheets TS of known thickness it is possible to adjust and fix the needed distance between electrode and sample. After the adjustment has been done the sheet must be removed in order not to hinder the vibrations. A cotton ring A serves as a seal for the internal atmosphere, for supporting the vibrating rod and also for suppressing horizontal vibrations.

When working with nonconductive samples a discharging surface procedure has to be used. This can be done by lifting the sample toward the electrode while at the same time short circuiting the electrode to the earth by use of the remote switch RS. The vibrating electrode was made from stainless steel and had a diameter of 2 cm.

A dessicant D could be used in order to maintain defined conditions in the internal atmosphere. For our experiments P_2O_5 has been used. All samples were of circular shape with a diameter of 2 cm or less, and thickness approx. 2 mm. The large surface was ground with 50 μm SiC powder. In some cases the sample surface was coated with silver by applying to it Acheson Silver Dispersion 915 directly by brush.

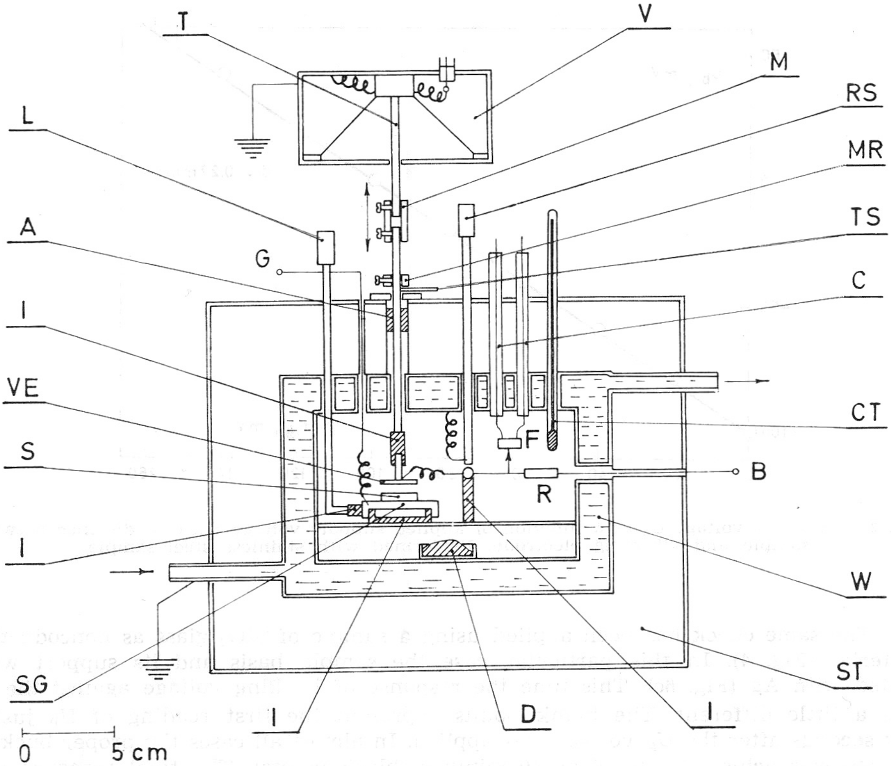

Fig. 2 — Thermostated sample cell for vibrating electrode experiments. T — vibration transmitter; L — device for lifting the sample support toward the vibrating electrode VE; A — pressed cotton ring; I — insulators, perspex or better; S — sample; SG — sample support; D — dessicant; ST — styrofoam insulation; W — double wall brass sink thermostated by water; CT — control thermometer; C — coaxial cables; TS — thin plastic sheet; MR — brass ring; RS — remote switch for discharging the electrode; M — brass connector; V — mechanic vibration source; F — FET transistor; R — 1000 M resistance; G and B — leads for external potential sources.

For experiments where a sample having electric bulk polarization was needed, a $BaTiO_3$ sample was used. This sample was prepared by hot pressing a mixture of $BaTiO_3$ powder and phenolformaldehyde resin. The sample of 42% $BaTiO_3$ (by volume), 28% resin, and 30% porosity[8] was treated in a D. C. electric field of 50 kV/cm at room temperature in a transformer oil bath for one hour in order to get a bulk polarization. The surface of the sample was carefully discharged from accidental charge by keeping it wrapped in an aluminium foil overnight, and by the discharging device of the sample cell before the beginning of the experiment.

Determination of Instrument Accuracy

In order to determine the instrument accuraccy a number of experiments were performed. Fig. 3. represents the bucking voltage U_b as a function of the external voltage applied at the sample support U_g. This measurement was performed on a conducting sample of stainless steel. It is evident that the change of bucking voltage follows precisely the change of U_g. The maximal deviation of points from the drawn line is about 3 mV.

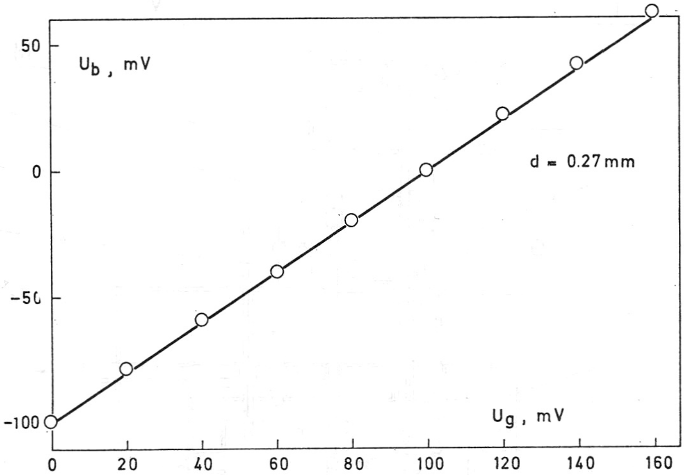

Fig. 3 — Bucking voltage U_b as a function of applied support voltage U_g. d — distance between sample and vibrating electrode. Performed with stainless steel sample.

The same check has been applied using a sample of SiO_2 glass as noncoducting material (Fig. 4). In this particular case the sample basis and its support were coated with Ag (Fig. 6c). This time the response of bucking voltage against the U_g was a little different. The blank points represent the first reading of U_b just a few seconds after the U_g voltage was applied. In almost all cases the proper bucking voltage was achieved after 5 or 10 minutes (black points). The final response and accuracy is the same as with the conducting sample. The maximal deviation is not more than 3 mV.

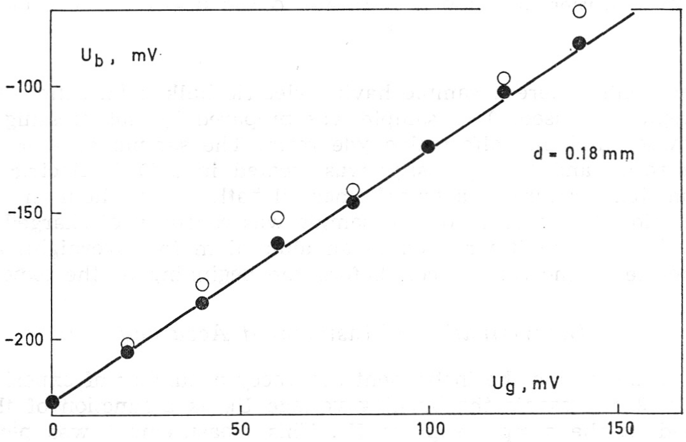

Fig. 4 — Bucking voltage U_b as a function of support voltage U_g. Performed with SiO_2 sample. d — distance between sample and electrode. Blank points — first response; black points — results obtained after 5—10 minutes.

In Fig. 5. the reading of the bucking voltage is plotted against the distance between the vibrating electrode and the sample surface. When the distance was less than 0.5 mm, the reproducibility of bucking voltage was good with deviations as small as 1 mV. For larger distances the scattering of results increased essentially up to 14 mV. For these measurements the stainless steel sample was used.

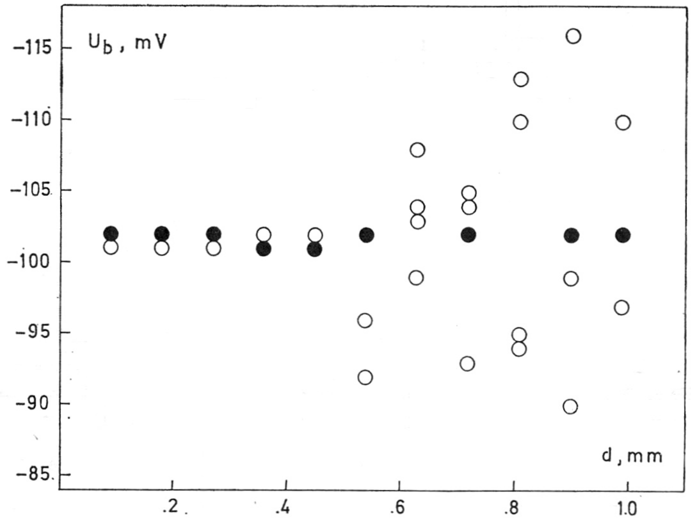

Fig. 5 — Bucking voltage against distance between sample surface and electrode d. Performed with stainless steel sample.

RESULTS AND DISCUSSION

Experiments with Metal Samples

In all experiments with metal samples a sample has been put on its support as shown in Fig. 6a. The bucking voltage U_b, equal to the measured potential, is the sum of potentials as shown in the following equation:

$$U_b = U_{t1} = U_{eg} + U_{gs} + U_{sa} + U_a, \tag{1}$$

where U_{t1} is the total measured potential, U_{eg} the sum of all the contact potentials which could appear at interfaces between the earth and the sample support, U_{gs} the contact potential between support and sample, U_{sa} the potential between sample and air, and U_a the sum of all other known or unknown contact potentials. The next measurement one can perform is the determination of a »blank potential« by measuring the total potential U_1^0 at the surface of the sample support (see Fig. 6b).

$$U_1^\circ = U_{eg} + U_{ga} + U_a, \tag{2}$$

here U_{ga} is the contact potential at the sample support-air interface. The difference between (1) and (2) results in:

$$U_{t1} - U_1^\circ = U_{s1} = U_{sa} + U_{gs} - U_{ga} \tag{3}$$

This is the simplest expression one can get. The experimentally obtained U_{s1} for a series of solid samples can characterize their solid — air interface only

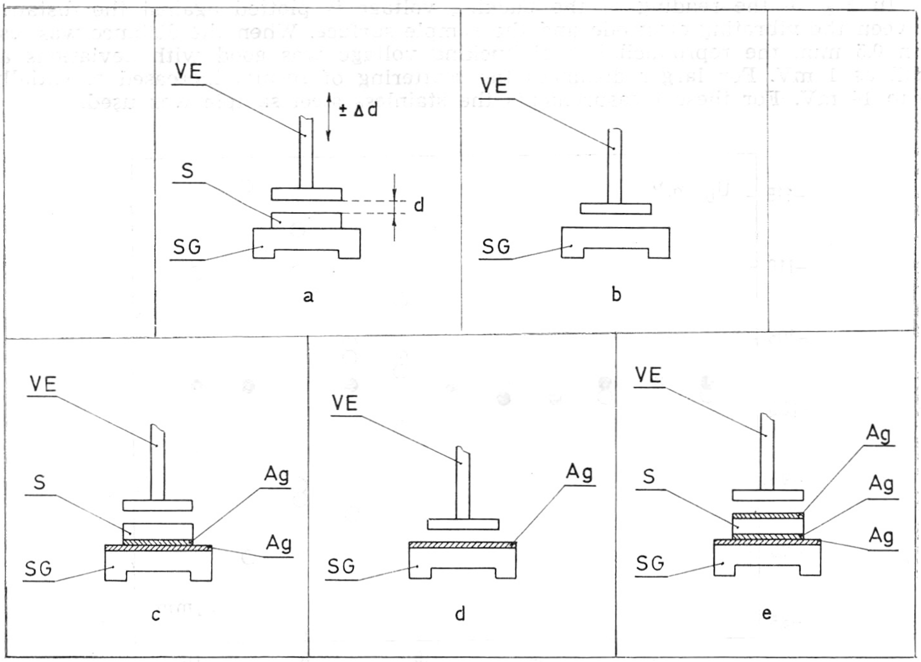

Fig. 6 — The positions of vibrating electrode against the sample and its support. SG — support; S — sample; VE — vibrating electrode; Ag — silver coating.

if the sample support and internal cell atmosphere is well defined and constant. Also, one of the two sample bases (the »lower« one) must not change from sample to sample, *i. e.* it must have constant characteristics for a series of samples.

Experiments with Insulators

Working with insulator samples one is confronted with some additional problems. In this particular case the position of the sample shown in Fig. 6a cannot be used. The sample surface as well as the support surface is not optically polished nor is any pressure applied in the direction normal to the sample surface. For that reason the adherence of the sample to its support will not be constant and reproducible. This fact will cause trouble and measurement is impossible. In order to make such experiments possible the »lower« surface of the sample has to be firmly coated by silver painting or some other conducting material. The support has also to be coated with the same coating. This situation is shown in Fig. 6c, and the bucking voltage (U_b) reading is given by:

$$U_b = U_{t_2} = U_{eg} + U_a + U_{gAg} + U_{AgAg} + U_{Ags} + U_{sa} + U_{bp} \qquad (4)$$

Here U_{t_2} is the total measured potential at the surface of the insulator, U_{gAg} the contact potential between the support and silver film. U_{AgAg} is the potential between silver coated support and silver coated sample, a value which must equal zero. U_{Ags} is the potential between silver coating and sample. The new value which must be taken into consideration when dealing with insulators is the potential caused by bulk electric polarization U_{bp}. For a dielectric without spontaneous polarization, U_{bp} is equal to zero. For other dielectrics the spontaneous polarization will directly influence the reading U_b. The corresponding blank experiment (Fig. 3d) will give the expression:

$$U_2^{\circ} = U_{eg} + U_{gAg} + U_{Aga} + U_a, \tag{5}$$

where U_2^0 is the potential at the sample support, U_{Aga} the contact potential at silver — air interface. The difference (4) — (5) is:

$$U_{t2} - U_2^{\circ} = U_{s2} = U_{Ags} + U_{sa} - U_{Aga} + U_{bp} \tag{6}$$

The U_{bp} value caused by bulk polarization can be determined by one additional experiment performed with the same solid dielectric sample. For that purpose the sample has to be taken out from the cell and its »upper« surface coated with the same coating as the »lower« one. A sample thus prepared and situated under the vibrating electrode can be seen in Fig. 3e. The measured U_{t3} value for the sample with the two applied coatings is given by:

$$U_{t3} = U_{eg} + U_{gAg} + U_{AgAg} + U_{Ags} + U_{sAg} + U_{Aga} + U_{bp} + U_a \tag{7}$$

If U_{AgAg} is avoided and U_{Ags} and U_{sAg} cancelled, the ordered equation is:

$$U_{t3} = U_{eg} + U_{gAg} + U_{Aga} + U_{bp} + U_a \tag{8}$$

By substracting U_2^0 (5), the new U_{s3} expression is obtained:

$$U_{s3} = U_{t3} - U_2^{\circ} = (8) - (5) = U_{bp} \tag{9}$$

Thus, we can see that vibrating electrode could be also used for measuring the bulk electric polarization of a sample. Of course, this method is valid under the assumption that both sample electrodes are equal, for only in that case U_{Ags} and U_{sAg} cancel.

The Experimental Check of Insulators Study

In order to confirm experimentally what was described in the previous discussion, the corresponding experiments have been performed. The results obtained can be seen in Table I. The result of experiment No. 1 represents the sum of contact potentials according to eq. (6). Knowing the structure of fused SiO_2 it is obvious that this sample does not have electric bulk polarization. Thus, the U_{bp} component is equal to zero. This fact is confirmed by experiments No. 2 and No. 3. Dealing with two electrode sample a zero result for U_{s3} had been expected. The two experiments actually gave 0.002 V and 0.007 V which is quite close to zero, considering the overall experimental uncertainty and a possible inequality of the electrodes.

The $BaTiO_3$ sample previously treated in a D. C. field was used in experiments No. 4 and No. 5. The corresponding U_{s3} results show the voltage caused by internal electric polarization. By turning the sample over the sign of the voltage is reversed due to the vector character of the polarization.

TABLE I

No.	Sample	Sample treatment	Measured potential according to eq. (6) or (9)
1	SiO_2 fused	Silver coated lower base (Fig. 6c)	+0.309 V
2	SiO_2 fused	Both bases were silver coated (Fig. 6e)	+ 0.002 V
3	SiO_2 fused	The same as No. 2, only the sample was turned over	+0.007 V
4	$BaTiO_3$ pressed powder	Both bases were silver coated (Fig. 6e)	—5.48 V
5	$BaTiO_3$ pressed powder	The same as No. 4. The sample was turned over	+5.37 V

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SAŽETAK

Upotreba metode vibrirajuće elektrode za karakterizaciju volumena i površine čvrstog tijela

M. Topić

Konstruiran je uređaj za mjerenje volta-potencijala koji postoji na površini čvrstih uzoraka. Umjesto referentne kemijske elektrode koja je obično spojena direktno za ispitivani uzorak, utjecaj same ćelije na mjereni rezultat eliminira se posebnim mjerenjem u ćeliji bez uzorka. Konstrukcija uređaja dozvoljava primjenu poznate razlike potencijala na površini uzorka, čime se vrlo točno može odrediti osjetljivost i točnost mjerenja.

Razvijene su posebne metode za mjerenje na vodljivim uzorcima kao i na uzorcima s izolatorskim svojstvima. Izvedene su relacije kojima se analiziraju eksperimentalno dobiveni rezultati za pojedine slučajeve mjerenja.

Posebna pažnja obraćena je uzorcima izolatora koji posjeduju volumnu polarizaciju. Pokazano je da unutrašnja polarizacija direktno utječe na rezultat mjerenja potencijala površine. Predložena je metoda za određivanje potencijala koji se javlja kao posljedica volumne polarizacije uzorka.

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