A Fixed Surface Potential Probe with the Swing Capacitive Electrometer Compared to the Vibrating Kelvin Probe

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Abstract— The novel fixed (non-vibrating) Volta potential probe was evaluated in comparison with the standard, vibrating (400 Hz) commercial Kelvin probe. While both tested probes demonstrated the similar behavior, there were significant practical advantages of the novel probe. Specifically, the novel probe allows for the elevated distance to the surface and provides more sensitivity to charge under the coating layer. These differences are explained by the analysis of probe circuitry together with the electrostatic approach to the dynamics of the Volta potential measurement.

I. INTRODUCTION

The capacitive probe method for the measurement of charge induced in the probe electrode was proposed by Lord Kelvin (W. Thomson) in 1898 as a capacitive quadrant electrometer switching between the immovable probe and discharge shunt while the biasing voltage is applied to the material specimen [1] (see Fig. 1(a)). The using of biasing voltage and thus the "zero signal" measurement were implemented because the capacitance of the quadrant electrometer is varied during the measurement and thus the measured value depends on the capacitance between the probe electrode and the surface of the specimen. Due to the manual switching and adjustment of biasing voltage, the using of original Kelvin probe was very time-consuming.. In 1932 the vibrating probe method was developed by W.A. Zisman [2] that allowed the use of an electronic amplifier and became widely known as a Kelvin probe (for example, [3-5]) illustrated in Fig. 1(b). Either in the capacitive quadrant electrometer or in the vibrating probe, the capacitance between the probe and specimen is varied and the induced charge is redistributed between this capacitance and parasitic capacitances between the specimen and probe relatively to the ground. The significant nonlinearity of the measured signal is mitigated by the application of compensating bias to the sample (or sample substrate) to reduce the measured signal to zero. Such a "zero point" measurement introduces the challenge of precious adjustment of biasing voltage at the very small output signal at the realistic electromagnetic background noise. Because the measured signal is, in fact, the derivative of varied electric charge, the very small gap between the probe and the specimen is required to keep the corresponding capacitance larger than parasitic capacitances.



Fig. 1 Transformation of Kelvin Probe: (a) Original capacitive quadrant electrometer of W. Thomson; (b) Modern scanning Kelvin Probe (top - SKP5050 from KP Technology, UK, bottom - scheme of KP 6500 from McAllister Technical Services, USA); (c) Micromechanical electrometer [6]; (d) Vibrating capacitor XL7900, Philips; (e) Varactor based electric field sensor [8].

In some application [6], probe electrode is not vibrating and the variable capacitor is installed inside of the probe in parallel to the fixed capacitor (typically the parasitic capacitance to the ground) as shown in Fig. 1(c). In fact, it is the micromechanical implementation of vibrating capacitor vacuum device XL7900 from Philips [7] (see Fig. 1(d)). The pure solid state (no mechanical parts) electrometer was proposed by M. A. Noras [8] utilizing the electric field modulated semiconductor structure (a varactor or metal-insulator-semiconductor structure) as shown in Fig. 1(e). While allowing for the immobilized probe electrode, all these devices (but original Lord Kelvin's probe) are producing the alternating current through the specimen due to the redistribution of charge between the varied probe capacitor(s) and fixed capacitance between the specimen and probe, which are connected in serials. While this is not an issue with the conductive object (very short relaxation time), the problem arises if the specimen is coated with the material, which dielectric constant depends on the frequency thus the measured signal depends on the frequency of vibrations. The investigation of this concern is the subject of presented work.

II. CONCEPT OF MEASUREMENT

Independently of the nature of surface potential (either the electrochemical, Fermi potential of the sample material or the localized space charge on the surface), the electrical potential over the surface is defined by the electric field of the space charge. This electric field induces the charge in the probe electrode as illustrated in Fig. 2, where the substrate of the specimen may be grounded or linked to the ground through the capacitance Csg = C specimen-ground and the surface of the specimen may be coated or uncoated that affects the capacitance Cps = C probe - specimen.



Fig. 2 The concept of measurement.

In the lump element presentation depicted in Fig. 2, all 3 capacitors (if present), C_{sg} , C_{ps} (either including the capacitance of coating layer or not), and the capacitance of probe transducer, C_p , are connected in serials. As a result, the electric field of the space charge, which would be equal to both directions in case of the ideal charged surface in the infinite space, redistributed between capacitor Csg and capacitors Cps and Cp connected in serials thus the electric potential of specimen's substrate relatively to the ground is equal for both branches. For the localized charge of trapped carriers, there is always energy barrier (and correspondingly the electric potential difference) between the charge and the bulk material of the substrate. The similar barrier is formed even in the ideal conductor or semiconductor where any localized surface states are absent as illustrated in Fig. 3.



Fig. 3. Illustration of space charge formed at the measurement of work function in metal (on left) and semiconductor (on right)

Therefore, the simulation model should be based on the conservation of charge while accounting for the redistribution of the electric field (and correspondingly the induced charge) in the measurement circuit. Our concept of the device is presented in Fig. 4 where the probe transducer contains the compound capacitor built from two capacitors, which are varied in the opposite mode (swing capacitor). The main idea behind this concept is to keep the constant total capacitance of transducer thus there is no charge oscillation outside of the transducer and probe is measuring the steady state induced charge similarly to the original device of Lord Kelvin.



Fig. 4.The evaluated concept of the device.

We have used the acoustic modulation to minimize the parasitic electromagnetic influence. Correspondingly, condenser microphones were used to build the swing capacitor. Because the modulated parameter is the distance between electrodes, i.e. the capacitance non-linearly depends on the excitation, the simulation of charge redistribution between the probe and specimen under the evaluation was performed with the Mathcad software. The capacitance of the non-exited microphone was set to 50 pF (a typical value for good quality condenser microphone and the distance between electrodes was modulated from 13% to 87%. The capacitance between the probe and object was set to 1 pF that corresponds either to the very small tip of the probe (high resolution) or relatively far distance to the object. The modulation frequency was set to 12 kHz. Results of this simulation are presented in Fig. 5.



Fig. 5. Simulation of processes in the swing transducer: (a) Variation of total capacitance between the object and ground; (b) Oscillation of charge in branches of swing capacitor, Q1 and Q2, and the total charge in the transducer; (c) Currents between branches of swing capacitor and the measurable differential current (red curve).

As Fig. 5 demonstrates, the variation of total capacitance does not exceed 1%, the total charge in the transducer is constant, and the current follows the modulation.

III. EXPERIMENTAL RESULTS.

The Fixed Electrode Kelvin Probe (FEKP), which is schematically presented in Fig. 4, was tested in comparison with the commercial Kelvin probe, CKP (KP 6500 from McAllister Technical Services). The FEKP transducer is show in Fig. 6 while Fig. 7 presents the experimental setup.



Fig. 6. FEKP transducer: (a) Sampler with brass electrodes (distance to the surface of sample - 1 mm); (b) Transducer in the sound-shielded case (open for the photo); (c) Disassembled transducer (left, acoustic part is normally placed on the top of right, "swing capacitor" part).



Fig. 7. Experimental setup for the linear scan with CKP or FEKP.

To evaluate and compare FEKP and CKP, we have used improvised, in-house fabricated samples of Aluminum alloy with coatings by epoxy primer and polyurethane paint. Some substrates were treated by electrolytic oxidation to generate the "corrosion" layer. Fig. 6 shows results of measurement for the resulting Volta potential with the evaluated FEKP and the CKP for bare substrate, the corroded (1 hour) substrate, substrate coated with the primer only, and fully coated substrate (primer and paint) without the "corrosion" and "corroded" during 1 hour and 5 hours. To mitigate differences in the material of probe tip (stainless steel in CKP and brass in FEKP), and the gain of electronics, measured data were normalized to match data for the bare metal substrate. , full OML layer and OML layers deposited on the substrates "corroded" during 1 hour and 5 hours., was tested with to reveal the magnitude and sign of corrosion produced space charge, with the results presented in Fig. 8.



Fig. 8. Normalized results of measurement with FEKP (Fixed Kelvin Probe) and CKP (Vibrating Kelvin Probe).

Fig. 8 clearly illustrate the advantage of a fixed, nonvibrating OPS probe over the standard, vibrating (400 Hz) Kelvin probe. The crucial difference is in the periodic redistribution of the electric field between the space charge and substrate and the varied capacitance between the space charge and Kelvin probe. Specifically, the measurement for the corroded only substrate (no coating) shows a comparable Volta potential for both probes (~30% difference) because the space charge in the corrosion layer is located on the surface of the sample, and the polarization time constant is small. The induced charge in the Kelvin probe almost follows the variation of the probe-to-surface capacitance. When the corrosion layer is covered by the primer and paint structure, the polarization time constant increases, which results in the only partial induction of a charge in the vibrating Kelvin probe.

To evaluate this explanation, we have performed the electrochemical impedance spectrometry (dry test) of the same polyurethane paint and epoxy primer- coated coupons. Results indicated that the coated material demonstrate a multipeak dielectric loss spectrum as shown in Fig. 9, where the imaginary part of capacitance (dielectric loss) is presented as the real part of the complex impedance.



Fig. 9. The real part of the complex impedance for the pain-on-primer coated samples:(a) Effect of corrosion under the coating; (b) Deconvolution of spectral components for the non-corroded sample.

Spectra in Fig. 9(a) show that the peak near ~ 700 Hz is revealed for all samples, including the sample coated without the preliminary oxidation while the oxidation notably reduces dielectric loss at lower frequencies. Deconvolution of spectrum for the nonoxidated samples in Fig. 9(b) reveals at least 3 main components with peaks at 6 Hz, 50 Hz, and 850 Hz. Comparing Fig. 9(a) and 9(b), the conclusion is made that the peak at 850 Hz should be attributed to the Aluminum Oxide film, which always exists on the surface of the Aluminum substrate. The electrochemically induced growing of this film doesn't change the position of the peak that indicates the polarization of bulk oxide in contrast to the interfacial polarization. In contrast, peaks at lower frequencies (6 Hz and 50 Hz) are associated with the polarization of the external coating. This explanation supports data obtained with the FEKP and CKP shown in Fig. 8: the low-frequency polarization of coating does not follow the commercial Kelvin probe vibration frequency (in our experiments, 420 Hz). In contrast, the fixed electrode probe allows for the full static induction of charge, which is measured by the internal swing electrometer. This explains why the FEKP always shows the higher Volta potential (i.e., the higher density of induced charge) if the original charge, to be detected, is located under the dielectric layer.

IV. CONCLUSIONS

The implementation of compound, "swing" capacitor in the transducer of fixed electrode Kelvin probe allows to minimize the redistribution of charge in the measurement circuit and thus to measure the established, steady state value of the induced charge. The preliminary experimentation with the fixed electrode Kelvin probe demonstrated that the top-coating notably reduces the potential reading by the commercial, vibrating Kelvin probe, while the fixed electrode probe's reading is much less affected.

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