SCANNING VOLTA POTENTIALS MEASUREMENTS OF METALS IN IRRADIATED AIR

H. S. Isaacs G. Adzic, and

[1]Energy Sciences and Technology Department
Brookhaven National Laboratory,
Upton, NY 11973, USA

C. S. Jeffcoate,
[2]The Ohio State University,
100 West 18th Av., Columbus, OH, 43210, USA

M. P. Ryan
[3]Imperial College of Science, Technology and Medicine
Prince Consort Road, London SW7 2BP, UK

A method for direct dc measurement of the Volta potential is presented. High intensity synchrotron x-ray beams were used to locally irradiate the atmosphere adjacent to the metal surface and produce a conducting path between a sample and a reference probe. The direct measurements of potential in the ionized air could be made at probe heights of around 1 mm compared to less than 0.1 mm for the Kelvin probe. The measurements were similar to traditional Kelvin probe measurements, but had a poorer spatial resolution. In contrast to the Kelvin probe methods, the approach described allows observation of the current as a function of impressed voltage. Methods to improve the special resolution of the technique and applications to corrosion under coating will be presented.

INTRODUCTION

Recently the scanning Kelvin probe has been employed, highly successfully, as a non-contacting technique for the measurement of Volta potentials in studies of corrosion [1-3]. A more spatially sensitive technique for scanning micron size areas has recently been developed based on an atomic force microscope [4] and has been used in corrosion studies[5] but not with a liquid covered surface. The scanning Kelvin probe consists of a vibrating micro-electrode close to a surface to produce a variable capacitance that induces an ac signal in the circuit directly connecting the probe and surface. Intrinsically, the method has a high impedance and necessitates both scanning close to the surface being studied, and care in shielding to reduce electrical noise. In contrast to the well known Kelvin probe method, direct (dc) measurements of the Volta or contact potential difference have been made in ionized air by Case and Parsons[6] and Smith [7]. In these studies a radioactive α emitting source was used to ionize the air between the reference metal/gas electrode and a gas/solution interface [6] or a second gas/metal electrode [7]. The present study extends x-rays have been used to produce an ionized gas for Volta potential measurements [8].

X-ray ionization of a gas is initiated by a primary x-ray absorption photoelectric process and is followed by ionization caused by ejected secondary electrons. Electron and fluorescent photon emission takes place in the gas around the site where the beam impinges on the metal and increases the ionization. Ionization by the electrons continues until they have lost their energy and attach to molecules. The process produces negative and positive gaseous charged molecules that combine and interact forming a range of products. Recombination of the ions and secondary electrons takes place rapidly as they diffuse from the path of the x-ray beam. The high concentration of charged species can be detected over distances of the order of a few 0.1 mm and depend on pressure and gas composition [9-11].

The present study again employs the dc ionized-air technique to measure the Volta potential of various metals with the view to applications in corrosion science. In our study we have used high intensity synchrotron x-rays to produce a local ionized atmosphere adjacent to the metal surface under investigation. These preliminary results have advantages over conventional Kevin probe methods which could greatly assist in making Volta potential measurements. In particular, Volta measurements using ionized air have been found to be relatively insensitive to reference/sample distances. Thus, the need for complicated electronics to maintain a constant height above the surface is avoided. Additional advantages are a relatively low impedance even with a small reference electrode, and the ability to carry out electrochemical (current versus voltage) polarization measurements of the metal/conducting-gas interface.

EXPERIMENTAL

Two multi-metal specimens were used. One consisted of the abraded edges of a series of metal sheets about 1 to 4 mm thick, pressed together in a holder. The metals were type 304 stainless steel, Al, Ni, Zr, Cu, Sn, and Fe. The second specimen was formed from an Al rod with a hole parallel to the axis of the rod in which a copper wire was placed. The rod was then swaged to bond to the copper wire. The final diameter of the Cu was 2.5 mm. The samples were abraded on SiC paper down to a 600 mesh. Care was taken during the final abrading of the cross sections of the sheets along their lengths to prevent cross contamination of adjacent metals. This could not be prevented with the Cu in the Al/Cu sample, but the measurements over the Al were on the leading side of the Cu disks where no Cu abrasion products would be present. The elemental metals contents were greater than 99.9%.

A schematic of the measuring setup for the beam at 45° to the sample is shown in Fig. 1. Samples were generally mounted parallel to the x-z plane of a stepper motor driven x-y-z stage with a minimum step size of 1 μm. The horizontal x and y directions were at 45^0 to the horizontal incoming x-ray beam. The vertical z direction was at 90^0 to the beam. A fixed microscope viewed the sample along the y-direction. The point of incidence of the beam was defined using a fluorescent sample with the surface in focus on this point. In one set of measurements, where the beam passed over the sample surface, the sample was mounted parallel to the beam and was scanned only in the z direction. The reference electrode probe remained static and within 0.1 mm from the beam except when effects of distance were investigated. Generally the reference probes were parylene coated, 0.25 mm diameter Pt-20% Ir alloy wires with exposed cross sections positioned 0.1 mm above the sample. Measurements with uncoated pointed Ag and Ni wire reference probes were also made with equal success.

The Volta potential between the sample and the probe was measured with a Keithley 614 electrometer or during polarization measurements, with a PAR 174 potentiostat (both having a nominal input resistance of 10^{13} ohm). For the polarization measurements a flat 3 mm diameter spiral of 0.5 mm Cu wire centered around the reference electrode served as the counter electrode. Volta potentials were also measured using an EG&G Scanning Kelvin Probe System 100E with a Ni scanning electrode having a tip diameter of 0.1 mm.

The measurements were made at Beamline X26A at the National Synchrotron Light Source. The beamline is designed for x-ray microprobe measurements using either monochromatic or polychromatic x-rays. The monochromatic beam has a photon flux of about 10^4 photons.$s^{-1}\mu m^{-2}$ for an x-ray ring current of 200 mA. The beam was focused to a diameter of close to 25 µm. The diameter of the polychromatic beam was about 8 µm with a flux of about 10^8 photons.$s^{-1}\mu m^{-2}$ having energies above 4 keV at a ring current of 200 mA [12].

RESULTS

Figure 2 shows a Kelvin probe scan in air over the sample consisting of a series of metal referenced relative to the Ni metal and two measurements made of the Volta potentials for the same sample in the ionized air created by an x-ray beam with a monochromatic x-ray energy of 6.1 keV with a Pt-Ir probe. Of the two measurements in ionized air, one scan had the beam impinging on the sample close to the probe and the other had the beam passing above and parallel to the surface adjacent to the tip of the probe. Comparison of the three curves demonstrates there is a clear relation between the potential variations measured with the Kelvin probe and the direct Volta potential measurements in the ionized air. Also there was no significant difference between the results with the beam above or impinging on the sample. For the three sets of measurements the potentials over each metal varied in accordance with the electron affinity and with its position in the galvanic series. This behavior has been noted previously by other investigators who showed a direct proportionality between the potentials in aqueous solution and the Kelvin probe measurements [1,5]. The distinct shifts in potential between the Kelvin probe and ionized gas measurements is due to a different reference potential. Potential changes with time have also been attributable to the reference electrode. For example scans over the multi-metal sample showed an average difference of 50 mV, indicating a distinct shift in the potential of the reference electrode, and a standard deviation of ±20 mV, because of noise. Complications in gas phase Volta measurements can be prevented by the correct choice of reference electrodes [12] for different gases and humidities. However, ionized gases contain free radicals and charges which could introduce chemical effects and electrostatic contributions which will be subject of future investigations.

The effect of increasing the distance between probe and sample was to reduce the spatial resolution. For example, at 0.5 mm above the multi-metal sample, the highest and lowest potentials were attenuated with the mean potential remaining approximately the same, i.e. about –0.6V. The decrease was about 15% in amplitude amounting to 150 mV between the potentials over the stainless steel and Al. At 1 mm the decrease in amplitude was about 50%.

Variations of the current with potential were measured with a potentiostat and a counter electrode over a Cu disk and over the Al in which it was embedded. The sample surface was freshly abraded on 600# SiC paper. A polychromatic x-ray beam impinged on the surface and a silver wire reference probe was positioned about 0.3 mm above this area. The resistance contribution in the gas phase was kept to a minimum by having the reference probe at a distance of about 0.05 mm and close to where the beam impinged on the sample. The results are shown in Fig.3. The open circuit potentials were consistent with the differences observed in Fig. 2. The slopes gave a minimum differential resistance around zero current and larger differential resistances at negative than at positive potentials. The Cu potential drifted with time as seen from the zero current potential for each potential scan at 5mV/s and then at 2 mV/s. The Al curves, measured after the Cu, showed very minor variations with time or scan rates. The behavior was only approximately linear. A linear response would indicate that the changes observed were due solely to "solution" resistance. Deviations from linearity and the minimum polarization resistance around zero current suggest that interfacial kinetics were controlling the current. These possibilities are being explored.

Fig. 4 demonstrates an application of the technique. A scan was made over an adhesive tape with a 0.5 mm hole on aluminum in a dry atmosphere. The scan showed high potentials of over 7 volts except over the hole and the edge and clearly identified the position of the hole. The high voltage was due to electrical charging of the insulating tape in the dry atmosphere. After exposure to 30 µl 1mM HCl the high potential dropped to over 5 volts where the vapors of the acid affected the surface of the tape. After removal of the tape the position of the corroded surface was also llocated because of a lower potential. In this case the potential variations were unaffected by surface charging.

DISCUSSION

In his review of equilibrium properties of electrified interfaces Parsons compared the measurement of the Volta potential with an ionized gas and that of a displacement technique when no current flowed [14]. The presence of the ionic phase must be expected to modify the interfacial processes. The degree to which any polarization takes place at the gas interface is uncertain and depends on the reactions, their kinetics and resistances of the ionic phase. Similar questions also arise when Kelvin probe measurements are made with polymer coated metals as it was clearly shown that the effects of the field between probe and sample were important [15].

The similarities in the changes in Volta potential with probe position across the multi-metal sample measured with x-ray induced gas conduction and a Kelvin probe are seen in Figure 2, demonstrating that the measurements in the conducting gas are dominated by the differences in the work functions. The conducting gas method has several advantages. Measurements can be made at heights of 1 mm; the probe to sample differential resistance is about 10^7 ohm (from polarization measurements) and requires no major shielding; and this technique can be used as an active probe for electrochemical measurements in the gaseous phase. In contrast, the impedance of a scanning Kelvin probe (with a probe area of a 1 mm^2, measured at a frequency of 100 Hz and a height of 10^{-3} mm) is greater than 10^{11} ohm. The Kelvin probe measurements are highly sensitive to probe to sample distance. Commercial equipment therefore incorporates scans of the surface to determine the variations in height before the work function measurements are made. The ability to make measurements at heights of over 0.1 mm is the major advantage in using ionized gas to make Volta measurements without contacting the electrode under study. This is expected to be of assistance with wet and coated surfaces and during high temperature oxidation of metals.

The potential variations in Fig 2 show that the Kelvin probe offers a superior spatial resolution of the contacting edges of the different metals. The derivative of these results gives negative and positive peaks with full widths at half the peak size of about 0.5 mm for the Kelvin probe and 1 mm for the ionized gas. The spatial resolution of AFM type Kelvin probes is of the order of 0.0005 mm and should be employed if spatial resolution of second phases is important. However, it cannot be used for in situ corrosion conditions.

Kelvin probe measurements are influenced by the proximity of a second metal [15] because of electrical fields. In conducting ionized gas, the reduced resolution may be more dramatic because of current flow arising from galvanic coupling of metals similar to those in aqueous solutions polarizing the interfaces with the gas phase. Literature measurements in conducting gases or plasmas were scrutinize for relevant data as Langmuir probes have been used for potential measurements at open circuit and with current flow. However, voltage levels of tens of volts or higher [17,18] were used for current measurements and were not directly applicable to the effects of metal contacts on the Volta potential in ionized gasses. In order to determine the magnitudes of the currents that flow, electrochemical polarization measurements were carried out. These are shown in Figure 3 and demonstrate that potential differences between different metals of about 0.5 V can produce currents of the order of 5 μA. Conversely, small currents flowing between different metals in contact in ionized air phase, could dramatically change the measured Volta potential and produce similar effects in the ionized air to those found in solutions. A consequence of the current flowing between the metals is much the same as the variations observed with a scanning reference electrode [19]. Under these conditions a single (mixed) potential is not achieved because potential differences arise due to ohmic potential (IR) drops, associated with the product of the flow of current (I) and resistance (R) of the ionic phase between the metals. The major difference between the aqueous solutions and the ionized air arises because of the limited range of the ions in air which restricts the distances between current sources and sinks and decreases the current magnitude and degree of localized polarization.

Fig. 4 shows an application of the technique. High voltages can be generated and consistently measured. Defects in coating discharge the voltages and greatly assist in locating defects in the coatings. In addition, the changes normally seen with Kelvin probe measurements over corroded areas of metals can also be clearly defined.

CONCLUSIONS

X-ray induced ionization of air has enabled Volta potential of metals to be measured directly with a high impedance voltmeter similar to measurements made in liquid electrolytes. The measurements are relatively insensitive to probe distances from the surface but the spatial resolution of surface differences is compromised because of galvanic coupling in the conducting gas.

Future studies will aim to improve the spatial resolution and will include measurements made in different gases, at different x-ray energies and fluxes. In addition, the effects of time and the kinetics of electrochemical processes taking place at metal surfaces in ionized gases environments will be examined.

ACKNOWLEDGEMENTS

This work was conducted at Brookhaven National Laboratory under the auspices of Department of Energy, Division of Materials Sciences, Office of Science under contract No. DE-AC02-98CH10886 and a Strategic Environmental Research and Development Program PP-1137/99 PP2-004F.

REFERENCES

1) M. Stratman and H. Streckel, *Corrosion Sci.*, **30**, 681 (1990).
2) A. Leng, H. Streckel and M. Stratman, *Corrosion Sci.*, **41**, 547 (1999).
3) S. Yee, R. A. Oriani and M. Stratmann, *J. Electrochem. Soc.*, **138**, 55 (1991).
4) Y. Martin, D. Abraham and H. Wickramasinghe, *Appl. Phys. Let.*, **52**, 1103 (1988).
5) P. Schmutz, and G. S. Frankel, *J. Electrochem. Soc.* **145**, 2295 (1998)
6) B. Case and R. Parsons, *Trans. Faraday Soc.* **63**, 1224 (1967)
7) T. Smith *J Applied Physics* 46, 1553 (1975).
8) G. C. Smith . J. Fisher and V. Radeka, *IEEE Trans. Nuc. Sci.* **NS-31**, 521 (1984).
9) H. S. Isaacs, C. S. Jeffcoate, A. J. Aldykiewicz, M. P. Ryan, M. Kaneko, G. Shea-McCarthy, *Electrochem. and Solid-State Letters*, **3**, 253 (2000).
10) J. D. Cobine, *Gaseous Conductors*, McGraw-Hill Book Co., Inc., 1941.
11) L. Katz and A. S. Penfold, *Rev. Mod. Phys.*, **24**, 28 (1952)
12) K. W. Jones, W. M.Kwiatek, B.M. Gordon, A. L. Hanson, J. G. Pounds, M. L. Rivers, S. R. Sutton, A. C. Thompson, J. H. Underwood, R. D. Giauque, and Y. Wu, in *Advances in X-ray Analysis*, C.V.Gilfrich, R. Jenkins, J. C. Russ, J. W. Richardson, Jr., P. K. Predecki, Edts., Vol. 31, Plenum Pub. Co., 1988.
13) R. T. Atanasoski, S-M. Huang, O. Alabani and R. A. Oriani, *Corrosion Sci.*, **36**, 1513 (1994).
14) R. Parsons in *Modern Aspects of Electrochemistry*, p. 103, J. O'M. Bockris Edt., Vol. 1, Butterworths Scientific Pub., London, 1954.
15) S-M. Huang, R. T. Atanasoski, and R. A. Oriani, *J. Electrochem. Soc.* **140**, 1065 (1993).
16) J. Bonnet, L. Soonckindt and L. Lassabatere,, *Vacuum*, **34**, 698 (1984).
17) L. Schott, in *Plama Diagnostics*, p. 668, W. Lochte-Holtgreven Edt., North-Holland Pub. Co.Amstercam, 1968.
18) F. C. Chen, in *Plasma Diagnostic Techniques*, p. 113, R. H. Huddlestone and S. L. Leonard Eds., Academic Press NY, 1965.

19) H. S. Isaacs and B. Vyas. In *Electrochemical Corrosion Testing*, p. 3, F. Mansfield and U. Bertocci, Editors, ASTM STP 727, 1981.

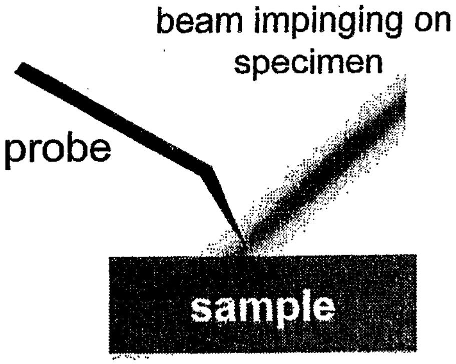

Figure 1. A schematic of the experiment for the measurement of the Volta potential of metals relative to a reference probe in ionized air. The air is ionized by the incoming high intensity x-ray beam from a synchrotron.

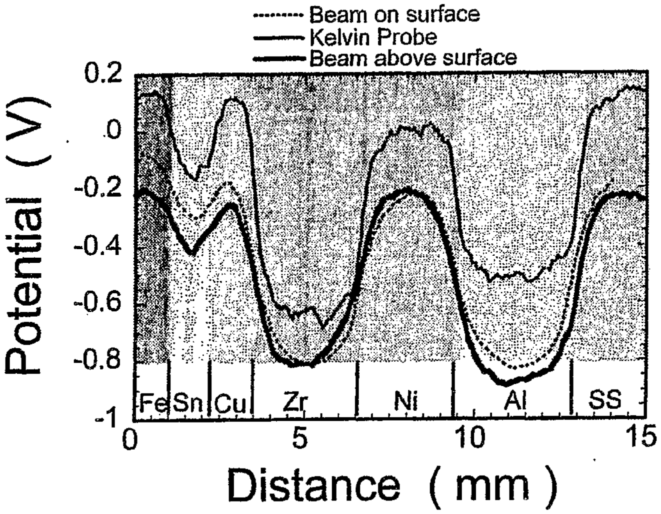

Figure 2. Scans showing Volta potential variations over a multi-metal sample.

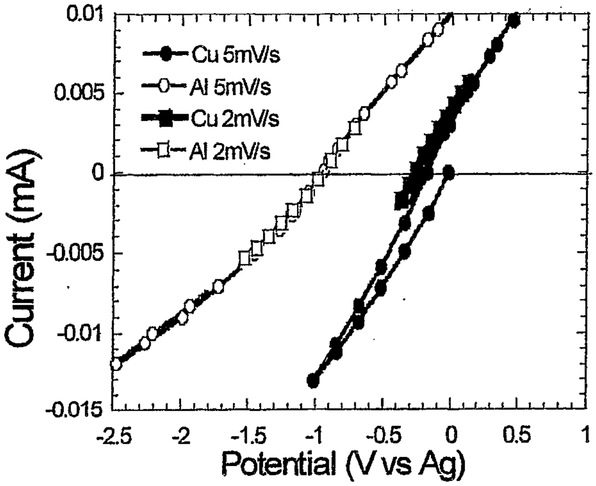

Figure 3. Polarization behavior of aluminum and copper in ionized air measured at 2 and 5 mV/s.

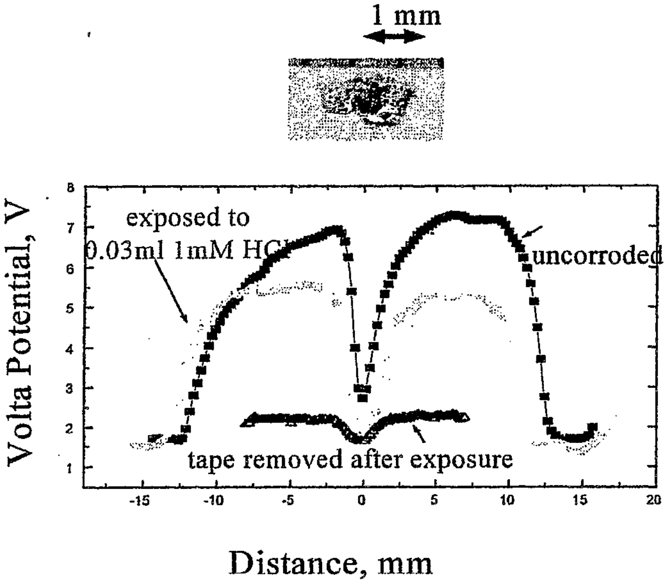

Figure 4. Scans over a hole in a tape on aluminum, before exposing to acid, after acid exposure and after the tape was removed.