SVET and LEIS: following and quantifying protection process

For the fast evaluation of modern high quality coatings new efficient methods are needed which provide reliable information in a short time about the protective features of the coatings. Electrochemical techniques are the potential candidate for such an application, particularly the modern scanning methods like the local electrochemical impedance spectroscopy (LEIS) and the scanning vibrating electrode technique (SVET). Within this work both methods were applied for testing differently pigmented protective coatings. By the development and optimisation of coatings a reliable and fast evaluation of their protective properties is necessary for the screening and choice purposes. The proven Florida or Arizona tests are extremely time consuming and for this kind of application useless. In order to shorten the investigation time, different accelerated short time tests can be applied (e.g. Salt spray test, weather-o-meter, Kesternich test, prohesion test etc.). As an alternative immersion tests in electrolytes, different cyclic tests and accelerated atmospheric exposures (SCAB) are being used. The remaining problems with these methods are their still too long duration, quantitative assessment of coatings and the correlation with the long time tests.

High sensitive methods monitored early corrosions stages
Modern scanning electrochemical measuring techniques like the local electrochemical impedance spectroscopy (LEIS) and the scanning vibrating electrode technique (SVET) can be of advantage by testing and evaluating the coatings. These methods operate on the basis of different working principles and allow both the evaluation of the corrosion related changes in the phase of the electrolyte solution close to the metal/coating phase (SVET) [1 to 3] or additionally the kinetic of the corrosion processes and the delamination of coatings (LEIS) [4 to 6]. For the efficient shortening of the testing time, artificial micro damages are inflicted to coatings and the corrosion and delamination related changes in the close vicinity of these places can be scanned with those methods. Due to the high sensitivity of these methods, the early stages of the corrosion and delamination progress at the damage of the coating can be monitored and the obtained data can be used for the fast evaluation/screening purposes.

LEIS and SVET
The thermodynamic state of the metal surface (active or passive), conversion or galvanic coatings, corrosion protective pigments or different binders can however, meaningfully influence the performance of LEIS and SVET. The purpose of this work was to evaluate the influence of these parameters by testing different pigmented protective coatings with LEIS and SVET.

Electrochemical activities visible with LEIS
To illustrate the sensitivity of SVET and LEIS, selected line scans for the untreated steel covered with a reference unpigmented coating are shown in Figure 1. The scans were taken over the midpoint of the artificial damage of the coating. In Figure 1 the different features of the SVET and LEIS scans are readily visible. With SVET, the damage location can be better recognised and the further deterioration of the coating at this place can be better followed. The LEIS data provide more resolved information about the electrochemical activities in the close vicinity to the damage. Analysis of the LEIS data for different distances from the midpoint of the damage provide the additional opportunity to discriminate the coatings.

The data of SVET potentials over the midpoint of the damage of the coating for the differently pigmented 2 pack epoxy hydro-primer on untreated steel are represented in Figure 2.

Zinc dust provides efficient cathodic protection
While three tested systems show certain potential changes, no considerable changes are visible for the zinc dust pigmented system. This kind of behaviour of the zinc dust is due to the efficient cathodic protection of the substrate and a fast conversion of Zn²⁺ to the insoluble ZnO. The iron mica pigmented and unpigmented systems take a middle position. The relatively high SVET potentials for the zinc phosphate pigmentation cannot be interpreted easily, since they can be either due to the electrochemical activity of the substrate or the soluble part of the pigment. Figure 3 represents the impedance data of the LEIS measurements for the same systems as in Figure 2.

Pigments protect metal outside of the damage
Two measuring points in the distance of 1mm and 5mm from the midpoint of the damage are taken into consideration. The strongest impedance loss and clearly the lowest impedance values are measured for the unpigmented sample. The data for the distance of 5mm from the midpoint of the damage reflect predominantly the barrier characteristics and the inhibition of the water and ion diffusion through the coating; these factors are influenced positively by the tested pigments. The impedance values for the short distance from the damage of the coating refer rather to the corrosion activity within the damage and its close vicinity. They reflect the distance protection of the coating on the one hand and the inhibition of the cathodic reaction in the vicinity of the defect on the other hand. It is evident that the zinc dust shows the best protection at a distance, in accordance with the SVET measurement. The action of iron mica should be however attributed to the suppressed cathodic reaction in the area close to the defect. The results of the SVET measurements for the tested systems on zinc-galvanised steel are plotted in Figure 4.

Active and barrier effects on zinc-galvanised steel
Remarkable for the data in Figure 4 is a relatively small corrosion activity of the substrate. The original activity for the zinc phosphate pigmentation is probably connected with the solubility of this pigment and the altogether small signals relate to the fast conversion of Zn²⁺ to ZnO. Similar as for the untreated steel, the LEIS data for the zinc-galvanised steel can be explained with both the active and barrier action of the coatings (Figure 5).

For the measurements conducted at a distance of 5mm from the midpoint of the damage a good barrier effect of zinc dust and iron mica is dominant. Regarding the results for the distance of 1mm both the active protection of zinc dust and the barrier effect of iron mica, strengthened by the easy oxidation of the zinc substrate within the cathodic area is evident.
Figure 6 shows the SVET data for the differently coated aluminium substrate. For this substrate no measurable electrochemical activities could be determined with SVET. On the other hand however the results of the LEIS measurements (Figure 7) for the same substrate show that the resolution of LEIS is sufficient for the discrimination between the tested coatings.

**LEIS shows differences in pigment behaviour even for sand-blasted steel**

It is well known that zinc has a negative electrochemical potential and consequently the passive status of the aluminium substrate (positive potential) can be disturbed. The effect of the galvanic coupling becomes apparent with the LEIS measurements at 5mm distance from the defect. In the vicinity of the defect, the necessary oxygen transport for the repassivation of the aluminium surface can take place, what is reflected by the higher impedance values for the distance of 1mm from the damage. The lower impedance values for zinc phosphate could be assigned to the effect of the soluble part of the pigment.

For the sand-blasted steel substrate, the SVET data do not reveal any considerable changes of the signal in the vicinity of the damage of the coating (Figure 8). It is evident that the good adhesive strength of the coating diminishes efficiently the cathodic reaction near the defect, so that the corrosion processes are no longer detectable with SVET. Examining the same systems with LEIS (Figure 9), it is still possible to discriminate between the different pigmentation.

**Correlation between short-time and conventional corrosion tests**

Outside of the area of influence of the defect, higher impedance values for the zinc dust than for the zinc phosphate and iron mica were found. This behaviour of the zinc dust results from the electrochemical (cathodic protection) and the physical barrier (oxidised zinc particles). Smaller impedance values for the zinc phosphate and iron mica can be connected either with the solubility or with a not optimal orientation of the pigment particles. The same interpretation applies to the data for the area close to the damage.

The results of the salt spray test for the untreated steel substrate in Figure 10 point out at a good correlation between the short-time electrochemical SVET and LEIS measurements and the conventional corrosion test.

**Cathodic reactions are limited by good barrier and adhesion properties**

For the purpose of a fast evaluation and screening of anti-corrosive coatings, artificial defects in the coating are introduced and the changes at these places as well as in their vicinity are followed under immersion in an electrolytic solution with the purpose to obtain preliminary information about the protective properties of the coating in an extremely short time. However, the electrochemical processes on the metal surface of the damage place which assist the coating damage are relatively complex and depend on several factors. If a coating is applied on an electrochemically active substrate (e.g. carbon steel), corrosion reactions in the defect are activated. Within a short time they lead to a spatial separation of the anodic reaction (Fe => Fe^{2+} + 2e^-) and the cathodic reaction (O_2 + 2H_2O + 4e^- => 4OH^-) which take place in the damage and in its close vicinity respectively. For the cathodic reaction, a diffusion supported transport of oxygen and water is crucial. Since the both reactions are in equilibrium, the slowest step of the two reactions determines the kinetic of the whole system.

If the coating exhibits good barrier properties or/and a good adhesion, both factors will limit the cathodic reaction and at the same time the corrosion within the defect. If the coating possesses active corrosion protection pigments which are able to impose a certain distance protection, this can lead to the inhibition of the anodic reaction in the defect. When testing coatings on passive substrates as aluminium alloys, no considerable corrosion reactions are detectable in the early stages of the exposition. Using SVET and LEIS, the processes discussed above can be followed and quantified. Since SVET is sensitive only for changes of the electrolyte phase due to the electrochemical processes like the anodic and cathodic reactions of an active metal, this method can be used for the investigation of uncoated and coated active metals. Concerning passive or easily passivated metals and alloys (stainless steels or aluminium alloys), the LEIS method offers more advantages, since with this method not only the changes in the electrolyte phase can be evaluated, but also changes on the metal surface and within the coating can be examined.

**Screening of corrosion protective pigments by SVET and LEIS**

SVET and LEIS represent an option for the fast investigation of different aspects of the corrosion protection of metals with coatings. Regarding different types of pigmentation of coatings, SVET and LEIS measurements can be used for the evaluation and screening of corrosion protective pigments. In the case of coatings on an electrochemically active substrate (e.g. carbon steel), both the active corrosion protection and the barrier effects can be determined quantitatively. For an efficiently working zinc dust pigment a complete cathodic corrosion protection is expected, which becomes apparent by small and constant SVET potentials within the area of an artificial defect of the coating. The application of SVET for the optimisation, formulation and quality control of coatings pigmented with zinc dust appears as advantageous.

**LEIS enquiry suitable for passive substrates**

By testing coatings pigmented with iron mica predominantly barrier effects can be expected, with a limited diffusion of water and ions throughout the coating. This inhibition effect on the cathodic reaction can be however partly or to high extent masked by the corrosion processes within the damage due to the lacking distance protection of this pigment. Since with LEIS both the area within the damage and in its vicinity can be resolved, it is well suitable in this case. With pigments that exhibit a certain solubility in water, certain difficulties can be faced by the analysis and interpretation of both SVET and LEIS data. In such cases measurements with complementary methods should be carried out.

Because the undercutting and delamination of coatings can be evaluated with SVET and LEIS, the testing of the adhesion of coatings can also be included into the investigation. The conducted SVET and LEIS measurements show that the surface state of the metal (untreated or sand blasted steel) can have a great effect on the corrosion protection. If the metal substrate is in a passive state (e.g. stainless steel or aluminium alloys), then LEIS suits usually better for the evaluation of coatings and protective pigments.

**References**


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Experimental
The working principles of SVET and LEIS are described in detail elsewhere [7 to 9]. The SVET and LEIS measurements were conducted by the same conditions with Model SVP100 and LEIS 270 from Uniscan Instruments, Buxton, UK. The distance between a probe tip and a substrate was 200µm by a vibration amplitude of 50µm (SVET) and a frequency of 1kHz (LEIS). The scanned area around the artificial defect with a diameter of 500µm was 10mm x 7,5mm. The electrolyte solution was 1mM NaCl and 1mM EDTA with a conductivity of 300µS/cm. The salt-spray-test was carried out according to DIN 53 167.

Four different substrates were chosen for the investigation, i.e. untreated carbon steel ST 14/05, zinc-galvanized steel type ST 14/05 and aluminium alloy AlMg 1, all from Chemetall GmbH, Frankfurt/Germany, and sand-blasted carbon steel ST 14/05 from Krüppel, Krefeld/Germany. As a coating two pack epoxy hydro-primer on the basis of "Beckopox 613" and "Beckopox 385", both from Vianova Resins GmbH & Co KG, Wiesbaden/Germany, were tested. The coatings were pigmented with such pigments as zinc aluminum polyphosphate hydrate ("Heucophos ZAPP"), iron mica ("Heucorox FL"), both from Heubach GmbH, Langelsheim/Germany, and zinc dust ("Zincoli Superfine 620") from Grillo Zincoli Germany, Stolberg/Germany. The pigments were used in coatings by Q = 20,55. As a reference the unpigmented coating was used. All coatings had a thickness of 21 ± 2µm.

Results at a glance
- Important information can be gained about the efficiency and the working principle of anti-corrosive coatings in an extremely short time by the investigation of artificial micro defects in coatings under immersion in an electrolyte solution.
- Electrochemical scanning methods such as SVET and LEIS are particularly well suitable for the investigation of artificial micro defects in coating. For the electrochemically active metal substrates SVET suits well. In the case of passive substrates and efficient barrier coatings, the use of LEIS appears as advantageous.
- SVET and LEIS are generally suitable for the preliminary evaluation of the active corrosion protection, barrier effects as well as adhesion and delamination of coatings within extremely short time periods.
Figure 1: SVET and LEIS line scans for the epoxy hydro-primer on untreated steel.

Figure 2: SVET data for the epoxy hydro-primer on untreated steel.
Figure 3: LEIS data for the epoxy hydro-primer on untreated steel.

Figure 4: SVET data for the epoxy hydro-primer on zinc-galvanized steel.
Figure 5: LEIS data for the epoxy hydro-primer on zinc-galvanized steel

Figure 6: SVET data for the epoxy hydro-primer on aluminum
Figure 7: LEIS data for the epoxy hydro-primer on aluminum

Figure 8: SVET data for the epoxy hydro-primer on sand blasted steel
Figure 9: LEIS data for the epoxy hydro-primer on sand blasted steel

Figure 10: Results of the salt-spray test on untreated steel according to DIN 53209 and DIN 53210 with the scale ranging from 0 to 5 for less corrosion and bubbles at 0 and high corrosion and numerous bubbles at 5