Application Note #000402

KeyWords
Acid, Catalysis, Corrosion, Metal,
XPS, Measurements, Surface Analysis

Corrosion study of a paper clip in vinegar with EnviroESCA

In this note we present (N)AP XPS results from the first comparative ex-situ and operando corrosion study on the reaction of commercial paper clips in concentrated vinegar solution containing 25% acetic acid.

Motivation

X-ray Photoelectron Spectroscopy (XPS) is a powerful and non-destructive technique for material and surface analysis, which provides quantitative elemental and chemical information. (Near) Ambient pressure (N)AP XPS has been developed to enable routine analysis of real world samples. The transformation of XPS from a UHV-based method towards environmental conditions has revolutionized XPS dramatically, and opened up many new application areas. (N)AP XPS is used extensively for in situ measurements and operando studies of industrial relevant (electro) chemical reactions and catalytic processes, especially at gas-liquid, gas-solid, and liquid-solid interfaces.

Steel is one of the most used materials in industry but its use in acidic environments can be affected seriously by corrosion. Acetic acid is a weak reducing acid and as one of the most relevant organic acids used in many industries. The effect of acetic acid on the kinetics of steel corrosion is a complex and serious problem.[1]

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as analytical technique, cf. Fig. 2. Here an electron beam is generated inside the X-ray source and focused on an aluminum X-ray anode. The deceleration of electrons on the anode generates X-rays. This X-ray beam is monochromated and focused on the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with a specific kinetic energy that is determined by their binding energy and the photon energy of the X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm are able to leave the surface.

These electrons propagate through the lens system of the electron analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The path of photoelectrons ends at an electron sensitive detector where the electrons are amplified and measured as intensity in counts per second.

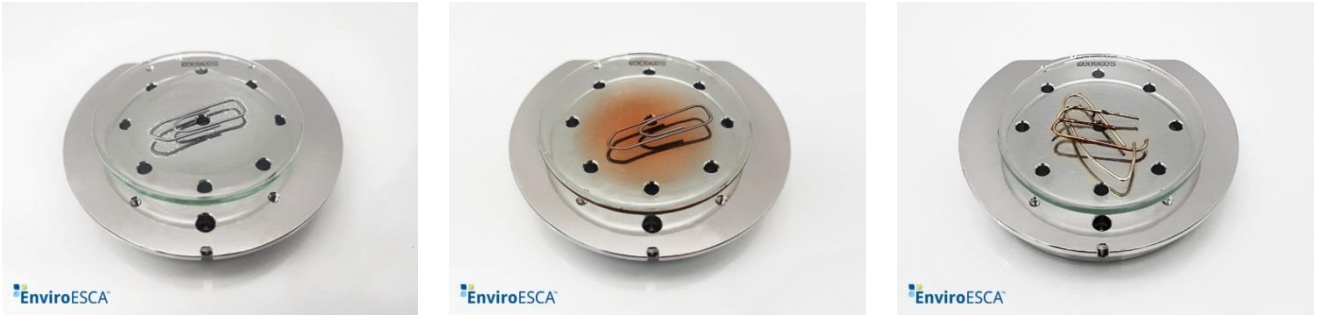

Fig. 1 Paper clip immersed in a concentrated vinegar solution (25 % acid) at different stages of corrosion (left and middle) and after complete evaporation (right) of vinegar solution.

A photoelectron spectrum is recorded by sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector. Then a quantitative analysis of the sample surface - giving the elemental composition - can be extracted from these spectra.

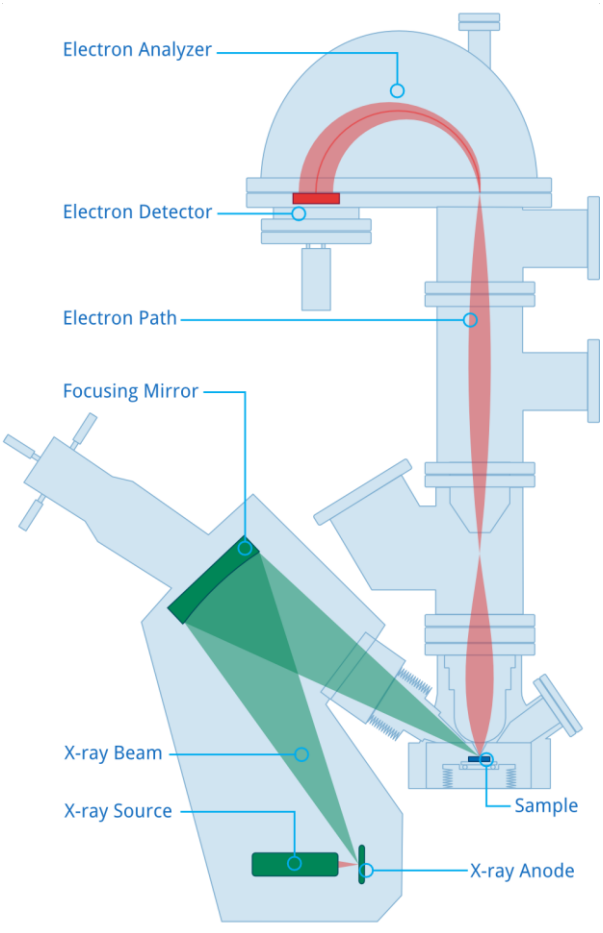

Fig. 2 XPS with EnviroESCA

Experimental Section

EnviroESCA can work under vacuum as well as (near) ambient pressure (N)AP conditions up to several dozens of mbar. Thus, it is very well suited to investigate (electro) chemical reactions at gas–solid or liquid–solid interfaces, e.g., corrosion of steel or metals.

EnviroESCA comes with an intrinsic charge compensation which we call *Environmental Charge Compensation* that makes additional low energy electron or ion sources unnecessary. As shown schematically in Fig. 3 illumination of the surrounding gas atmosphere with soft X-rays generates free charges, which compensate potential surface charging on the sample.

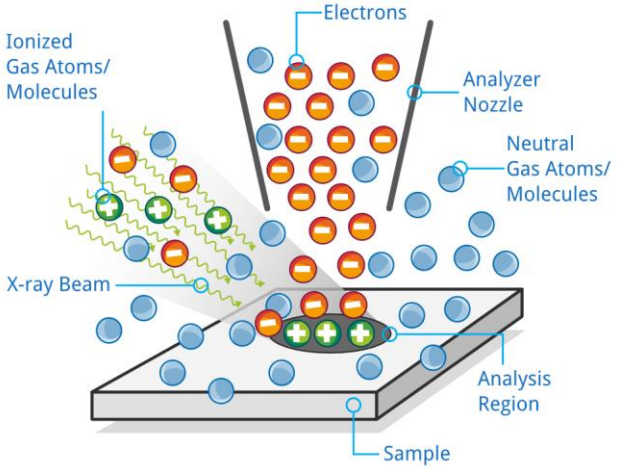

Fig. 3 Environmental Charge Compensation

The (N)AP-XPS capability of EnviroESCA allows in situ and operando studies of a multitude of samples in very different environments.

Here, we present results of a surface chemical analysis of a commercial paper clip before, during and after immersion in a concentrated vinegar solution (25% acid) using the EnviroESCA, see Fig. 1. In the following section XPS data will be presented that have been obtained from the paper clip after:

1. 0.5 h sonication in *iso*-propanol (^{i}PrOH),
2. 2 h immersion in vinegar at 9 mbar, and
3. 12 h in vinegar at ambient pressure.

Results

As a first reference we analyzed a native paper clip, which was cleaned in *iso*-propanol by sonication for 0.5 h to remove any unintended adventitous contaminations originating from prior handling or the manufacuring process. The obatined survey spectrum of the cleaned paper clip is shown in Fig. 4 as blue curve.

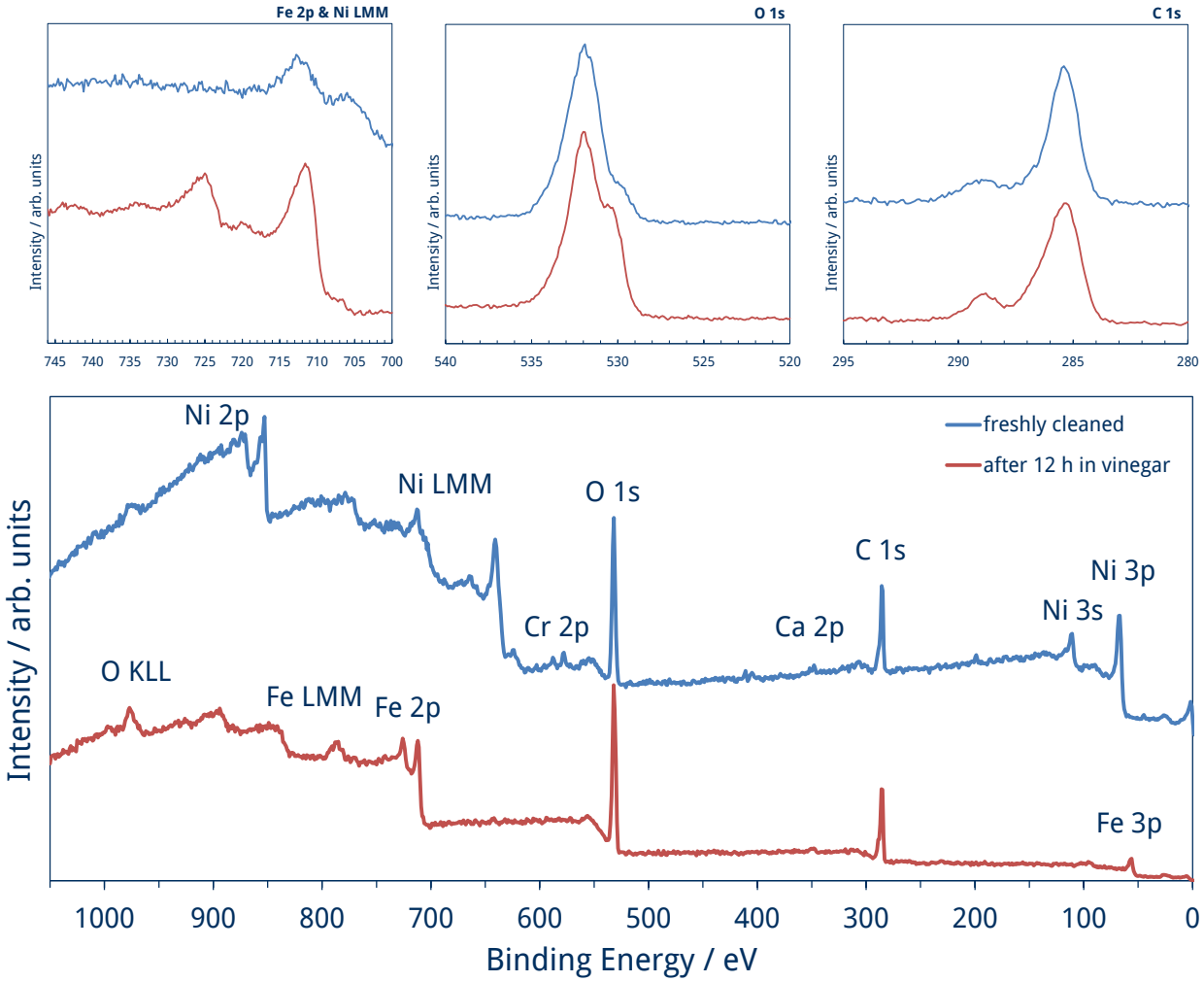

Fig. 4 Survey and detail spectra of a paper clip after 0.5 h sonication in *iso*-propanol (blue) and after 12 h immersion in a concentrated solution of vinegar (red).

On a freshly cleaned clip nickel together with oxygen and carbon could be detected with additonal very small contributions originating from chromium and calcium. Other commercial clips are made from differnt steel types, which show also Mn and/or Zn. Here we will foucs on the pure nickel (chromium) steel clip. The corresponding detail spectra (Fe 2p, O 1s, C 1s) of the clean clip are shown as blue curves in Fig. 4.

Then the paper clip was immersed in vinegar solution and transferred into the EnviroESCA. Next XPS was done live in the EnviroESCA directly on the clip in contact with the acidic liquid at 9 mbar, as shown in Fig. 5. Here again Ni, O, and C are the predominant elements in the beginning but after 3 h immersion also a small Fe 2p peak becomes apparent (*cf.* Fig. 6).

Prolonged immersion of the clip in vinegar yields a brownish colored solution and a solid brown residue is found on the clip and in the glass after complete evaporation of the liquid, see Fig. 1. After 12 h in vinegar concentrate the survey spectrum looks completely different, which is illustrated by the red curve in Fig. 4.

Now iron apart from oxygen and carbon is the main constituent of the survey spectrum. These changes on the paper clip surface due to acidic corrosion are also visible in some of the detail spectra, e.g., in the Fe 2p and O 1s core-level shown in Fig. 4. Some of the studied clips showed also a small copper signal after 12 h immersion in vinegar.

Fig. 5 Paper clip immersed in a concentrated vinegar solution (25 % acid) in the sample environment (left) and during live acquisition at 9 mbar under the nozzle (middle, right) of EnviroESCA.

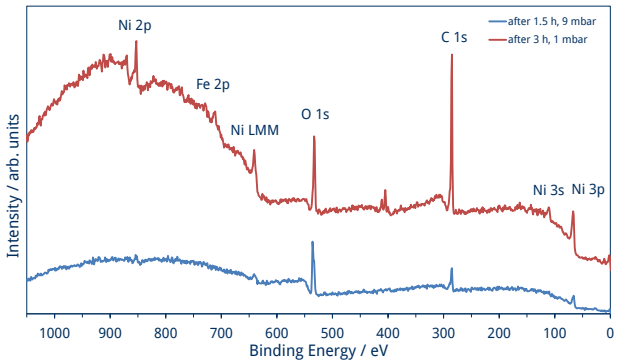

Fig. 6 Operando NAP XPS survey spectra of a paper clip during immersion in a vinegar solution for 1.5 h (blue) and after 3 h (red).

Analysis of the C 1s core-level spectra exhibits the presence of additional carbon species in the used vinegar solution. These CC/CH related peak components located at 285.0 eV can be assigned to hydrocarbons, which are not originating from acetic acid (CH_3COOH) but might be some by-products of vinegar production.

That finding is corroborated by C1s spectra of pure acetic acid (*cf.* green curve in Fig. 7) showing only two peaks at with a sepeartion of 3.5-3.8 eV originating from its CH_3 (~287.5 eV) and COOH (~291.0 eV) moiteies as expected.[2-5]

C 1s spectra of the brown solid (*cf.* brown curve in Fig. 7) are also composed only of those two peak components, which suggests the formation of iron acetates.

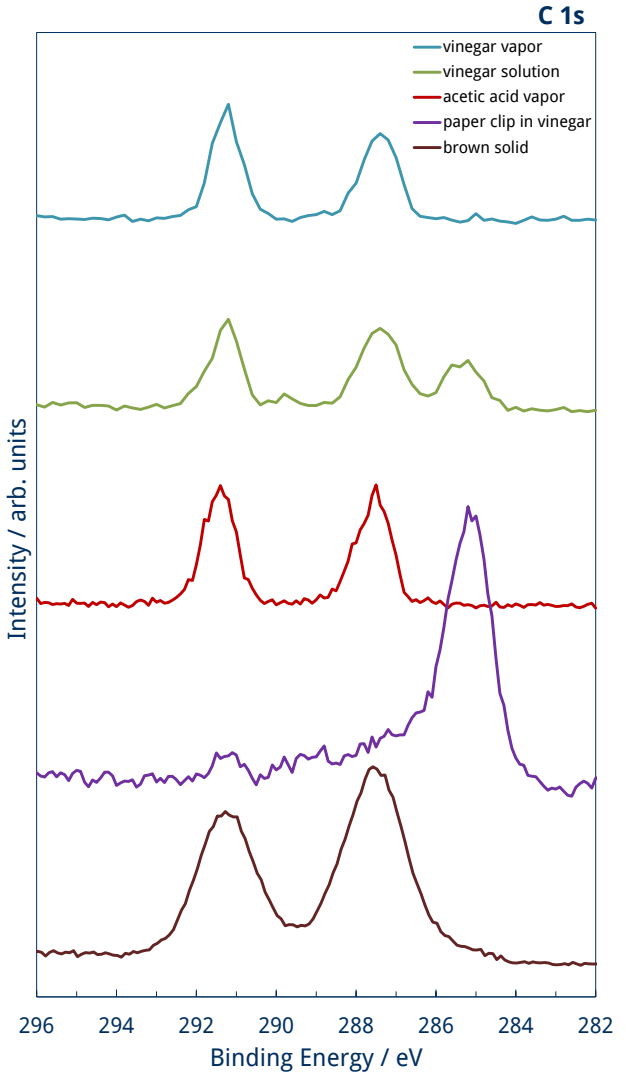

Fig. 7 C 1s core-level spectra of from top to bottom: vinegar vapor, vinegar solution, acetic acid vapor, paper clip in vinegar, and the brown solid. All spectra were acquired at 9 mbar except for the brown solid, which was obtained at 1 mbar.

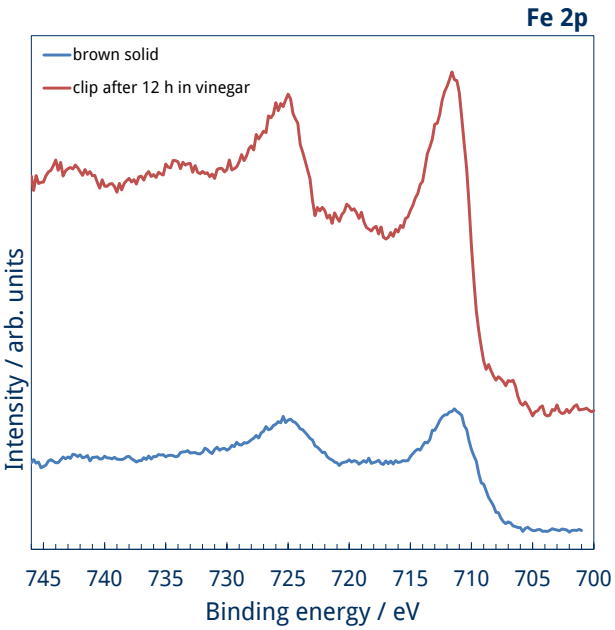

Fig. 8 Fe 2p spectra of a corroded paper clip after 12 h immersion in vinegar (red) and the brown solid (brown).

Conclusion

The unique capabilities of EnviroESCA to work in (near) ambient pressure conditions using different gaseous and liquid environments allows manifold studies – in-situ as well as operando – of various gas-liquid, gas-solid, and liquid-solid interfaces.

Here we present a comparative ex-situ and operando corrosion study of commercial paper clips in a concentrated vinegar solution containing 25% acetic acid.

Since the real composition of the studied paper clips is unknown, only small details of the bigger picture of their acidic corrosion in vinegar could be obtained. The main thing we learned is that iron is enriched on the surface of the paper clip within the progress of corrosion in aqueous vinegar solutions. And that the nickel signal is attenuated completely by that iron-rich surface layer.

Moreover, XPS analysis of the red-brown crystalline residue that forms around the paper clip after complete evaporation of vinegar solution, suggest the formation of iron(II/III) acetates as a (by)product (see C 1s and Fe 2p spectra in Fig. 7–8).

The reaction of iron with vinegar, respectively the acetic acid, results in a brown solution with iron(II) and iron(III) acetates. Additionally, iron(II and/or III) (oxy)hydroxides might be formed, which then also react with the vinegar's acetic acid to form iron acetates.

Quantitative XPS of the brown solid gives an elemental composition of 51.6 atom% oxygen, 41.1 atom% carbon, and 7.3 atom% iron. These numbers suggest that iron(III) acetate* with a chemical composition of O 51.5 atom%, C 40.0 atom%, and Fe 8.5 atom%) is one product of the herein studied corrosion of paper clips made of nickel (chromium) steel in aqueous vinegar solutions with 25% of acetic acid.

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*Iron(III) acetate: chemical formula $C_{14}H_{27}Fe_3O_{18}$

Videos showing live acquisition of XPS spectra on the clip in vinegar at 9 mbar can be found on our web site. www.enviroai.com