

## TRIBOCORROSION ON DIAMOND LIKE CARBON COATING



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## INTRODUCTION

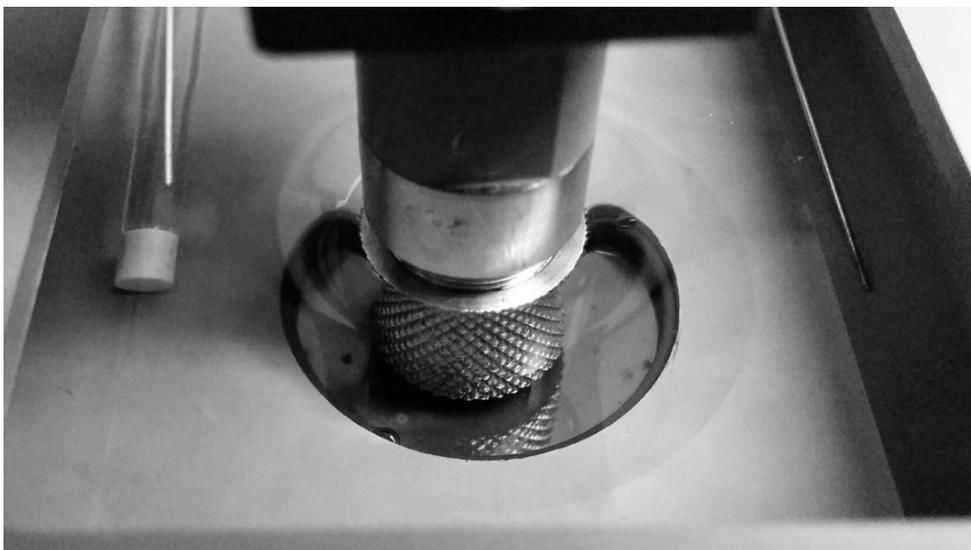
Diamond-like carbon (DLC) coating is a nanocomposite coating that displays some of the properties of diamond such as high hardness and low friction. DLC coatings exist in seven forms, which possess  $sp^3$  and  $sp^2$  hybridized carbon atoms. DLC coatings with more  $sp^2$  bond type are softer, while the ones with predominant  $sp^3$  bond type exhibit higher hardness. Desired mechanical and tribological properties can be obtained by tailoring the  $sp^2$  and  $sp^3$  carbon and hydrogen concentration. The combination of excellent wear resistance and very low friction of DLC makes it an ideal protective coating for different industrial applications, such as razor blades, metal cutting tools, bearings, motorcycle engines, as well as medical devices, due to its superior bio-compatibility.

### IMPORTANCE OF TRIBOCORROSION TESTING ON PROTECTIVE COATINGS

Tribocorrosion is a surface degradation process resulting from simultaneous tribological and electrochemical actions in a corrosive environment [1-4]. The corrosion process can cause material degradation, and affect its friction, wear and lubrication behavior [2], i.e. DLC coating in this study. For example, the lifetime of the DLC coated replacement hip joints and artificial knees can be significantly reduced by the corrosive environment of the body fluid. The Tribocorrosion Module of the Nanovea Tribometer provides an ideal tool to assess the corrosion and wear behavior of the protective coatings in a controlled and quantitative manner.

### MEASUREMENT OBJECTIVE

The tribocorrosion process of the DLC coatings on different types of steel substrates is simulated using the Nanovea Tribometer. In this study, we would like to showcase that Nanovea Tribometer equipped with the Tribocorrosion Module is an ideal tool for evaluating the performance of protective coatings used in wear and corrosion environment.



**Fig. 1: Setup of the tribocorrosion module.**

## TEST PROCEDURE

### SAMPLE DISCRIPTION

Diamond like carbon (DLC) coatings coated on different steel substrates were used for this study. The steel substrates include a low alloy steel and a tool steel for comparison. The tool steel has a better corrosion resistance and higher hardness. The DLC coating has a thickness of ~2  $\mu\text{m}$ . The identifications of the tested samples in this report are listed in Table 1. Due to the agreement with the client, the detailed information of the coating and substrate is not disclosed in this report.

Sample ID	Structure
Sample 1	DLC on Low alloy steel
Sample 2	DLC on tool steel

**Table 1: Summary of samples for testing.**

### TRIBOCORROSION TEST

#### Tribocorrosion test at Open Circuit Potential

Nanovea Tribometer equipped with the Tribocorrosion Module of electrochemical impedance spectroscopy (EIS) addition was applied to evaluate the tribocorrosion behavior. The sample was fixed against an O-ring with a surface area of 4.91  $\text{cm}^2$  exposed to 1 wt.% NaCl solution at room temperature. The sample, a platinum wire and a Ag/AgCl, NaCl (sat'd) electrode were used as working, counter and reference electrodes, respectively. A normal force of 30 N was applied using an  $\text{Al}_2\text{O}_3$  ball of 6 mm diameter. The Open Circuit Potential (OCP) was monitored by a potentiostat throughout the tribocorrosion experiments. The sample was first kept in the electrolyte for 1 h to obtain a stable OCP, followed by the tribocorrosion test for 30 min. After the wear process, the sample was kept in the solution for another 20 min to allow surface repassivation. Electrochemical impedance spectroscopy analysis was performed to compare the corrosion resistance of the sample before and after the wear test. Dry wear tests were also performed at the same condition for comparison. The wear track morphology was examined by an optical microscope. The test parameters are summarized in Table 2.

Test parameters	Value
Normal force	30 N
Reciprocating speed	1 Hz
Duration of wear	30 min
Wear track length	5 mm
Revolutions	1800
Ball Diameter	6 mm
Ball Material	$\text{Al}_2\text{O}_3$
Electrolyte	1 wt.% NaCl
Temperature	24°C (room)
Humidity	40%

**Table 2: Test parameters of the tribocorrosion measurement.**

### **Tribocorrosion test at Controlled Potentials**

In order to further investigate the effect of corrosion reactions on the tribocorrosion properties of the coating-substrate system, the wear tests were carried out under anodic polarization conditions, while the other test parameters listed in Table 2 were kept the same. A +0.5 V potential vs. OCP was applied to Sample 2 to accelerate the corrosion process while the evolution of the current was monitored before, during and after the wear process.

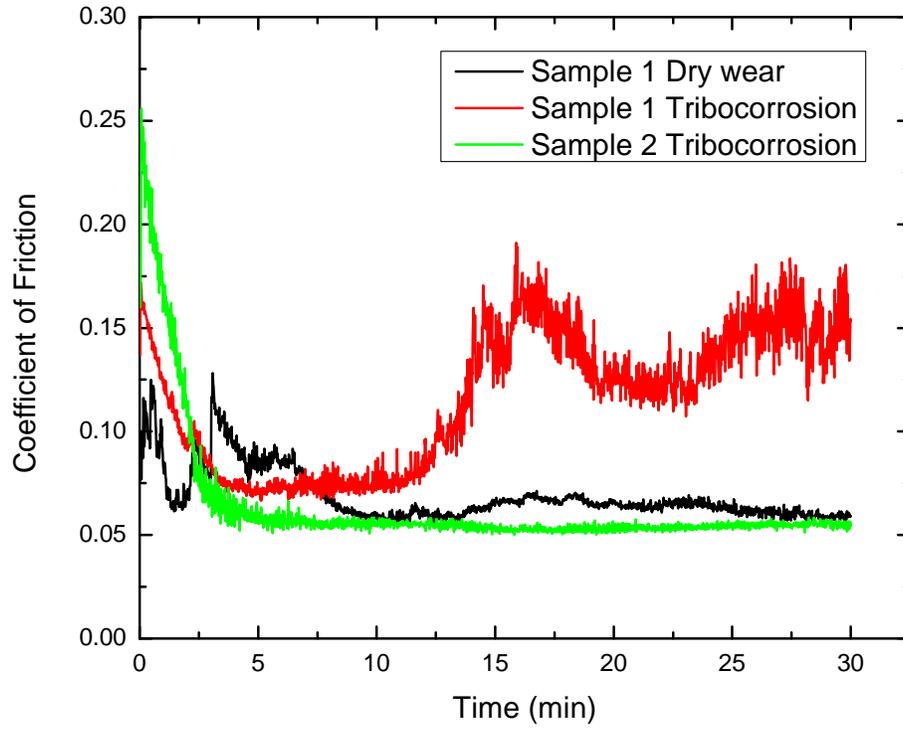
## **RESULTS AND DISCUSSION**

### **Tribocorrosion test at Open Circuit Potential**

The coefficient of friction (COF) was recorded in situ during the wear tests at different conditions as shown in Fig. 2. Sample 1 shows a stable low COF of ~0.06 after the run-in period in the first 10 min during the dry wear test. Such a low COF is attributed to the formation of a self-lubrication tribolayer. In comparison, the wear test of Sample 1 performed in the corrosive NaCl electrolyte shows a relatively higher COF above 0.12 after 12 min wear, which may be related to the failure of the DLC coating during the tribocorrosion process. The presence of the corrosive electrolyte accelerates the mass loss due to the synergistic effect of corrosion and wear. Sample 2, which has a steel substrate with better corrosion resistance, shows a low COF of 0.05 during the tribocorrosion test.

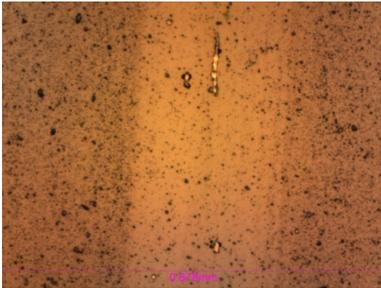
Fig. 3 shows the micro images of the wear tracks after the tests at different conditions. As shown in Fig. 3a, Sample 1 tested in a dry environment exhibits a smooth wear track where the coating is still present and protects the substrate. On the other hand, Sample 1 tested in the corrosive media exhibits a wear track with exposed metal substrate. In comparison, the DLC coating remains protective after the 30 min tribocorrosion test for Sample 2, which has a more corrosion resistant steel substrate.

The surface of Sample 1 after the tribocorrosion test was further examined under the microscope as shown in Fig. 4. It can be observed that pits of different sizes formed on the surface of Sample 1. During the tribocorrosion test, the corrosion medium ( $\text{Cl}^-$  ions) penetrates through possible microdefects in the DLC coating, and rapidly attacks the steel substrate underneath and creates small deep pits. The severity of the localized corrosion attack at this stage mainly depends on the corrosion property of the substrate. When the steel substrate progressively dissolves and becomes unable to provide sufficient support, the DLC coating is removed by the wear process. Such finding illustrates that the corrosive medium plays an important role in weakening the protective coating system during the tribocorrosion process.

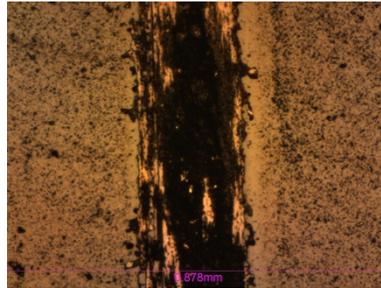


**Fig. 2: Evolution of COF during the wear tests.**

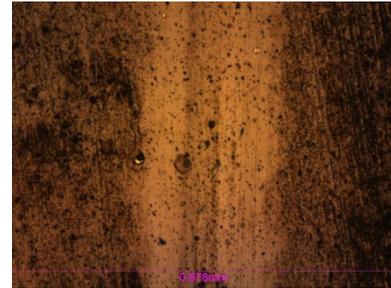
(a) Sample 1  
Dry wear:



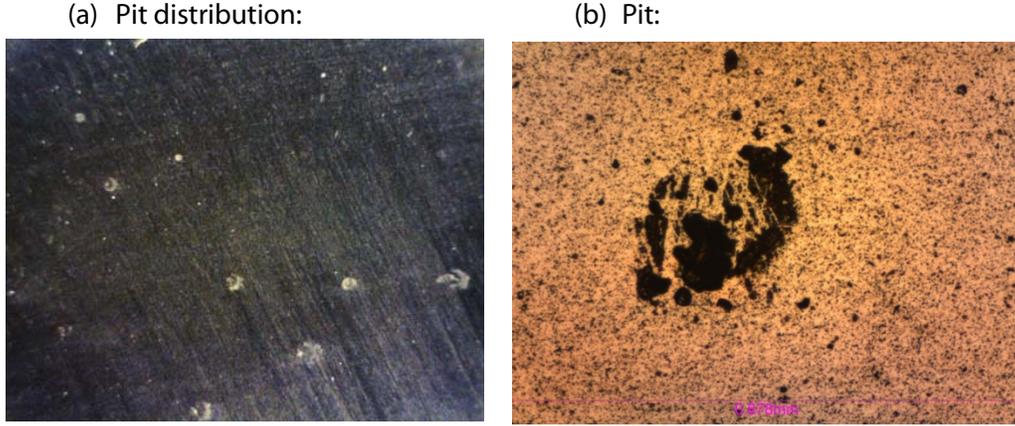
(b) Sample 1  
Tribocorrosion:



(a) Sample 2  
Tribocorrosion:



**Fig. 3: Images of wear tracks after the wear tests.**



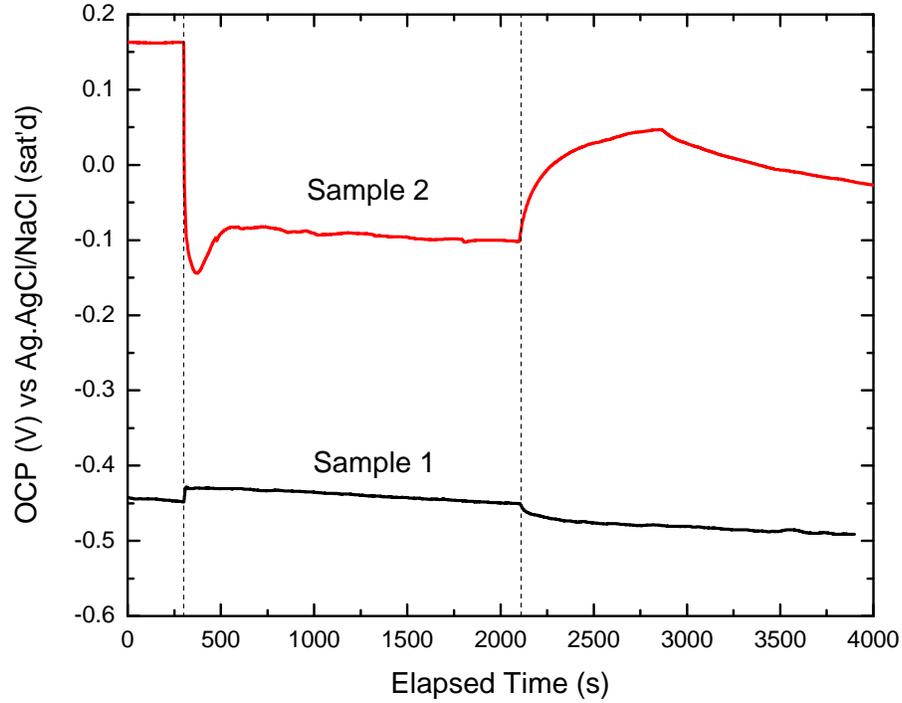
**Fig. 4: Pits of Sample 1 after tribocorrosion at OCP.**

Evolution of the OCP before, during and after wear tests on Sample 1 and Sample 2 is presented in Fig. 5. The OCP of Sample 1 maintains a lower value compared to Sample 2. EIS tests were performed at OCP to quantitatively characterize the corrosion resistance of Sample 1 and Sample 2 before and after the tribocorrosion tests. The Nyquist Plots of the EIS of Sample 1 and Sample 2 are compared in Fig. 6 and the best-fit values of the Randle equivalent circuit are summarized in Table 3. As shown in the insert of Fig. 6b, Randle circuit consists of the following components: solution resistance,  $R_s$ , in series with a parallel combination of the charge transfer resistance,  $R_{ct}$ , and of  $Q_{dl}$ , which is a constant phase element corresponding to the double layer capacitor. The latter parameter replaces the capacitor  $C_{dl}$  to account for a deviation of the impedance from the pure capacitor behavior due to surface inhomogeneities. It can be expressed using the following equation:

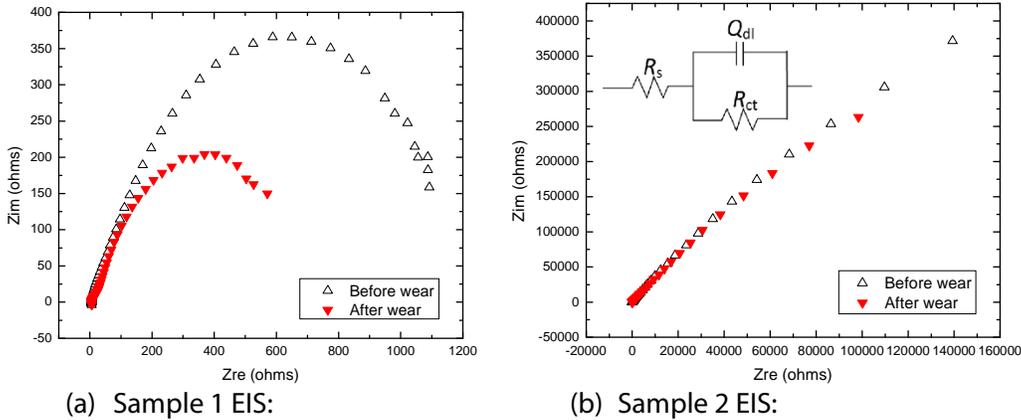
$$Z_Q = 1/[Y_0(j\omega)^n],$$

where  $Y_0$  is the constant of  $Q_{dl}$ ,  $n$  is the empirical exponent of  $Q_{dl}$  representing the degree of deviation of  $Q_{dl}$  from pure capacitor, and  $\omega$  is the angular frequency.

The  $R_{ct}$  value, representing the corrosion resistance, of Sample 1 is reduced from 1211 to 929  $\Omega$ , attributed to the synergistic attack by corrosion and wear during the test. This is also confirmed by the constant decrease of the OCP throughout the tribocorrosion test and widely distributed pits on the surface of Sample 1. In comparison, Sample 2 shows a comparable  $R_{ct}$  of  $\sim 2.4 \times 10^6 \Omega$  before and after the tribocorrosion test, which is more than three orders of magnitude compared to that of Sample 1. It exhibits no pits after the test. These evidences demonstrate an excellent tribocorrosion performance of the coating-substrate system of Sample 2. Besides the protective coating, the corrosion resistance of the substrate also plays a critical role in the general tribocorrosion application. This is especially important in a corrosive medium of  $Cl^-$  ions, where pitting corrosion is the predominant corrosion mechanism.



**Fig. 5: Evolution of OCP before, during and after the wear tests.**



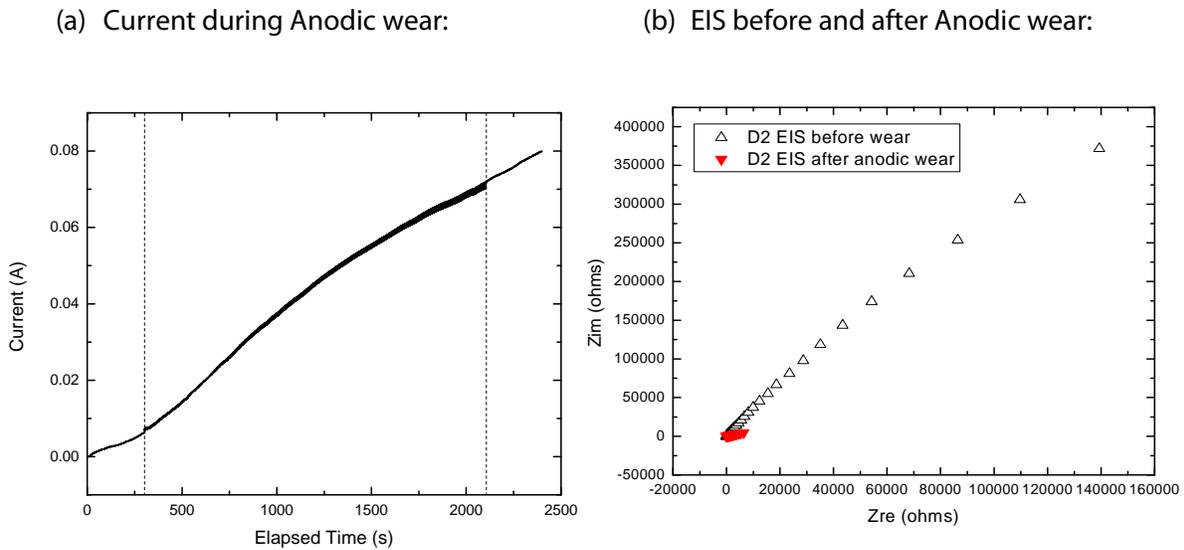
(a) Sample 1 EIS: (b) Sample 2 EIS:  
**Fig. 6: EIS Nyquist plots of Sample 1 and Sample 2 before and after tribocorrosion.**

	$R_s$ ( $\Omega$ )	$Q_{dl}$ -Q (F)	$Q_{dl}$ -n	$R_{ct}$ ( $\Omega$ )
Sample 1 EIS before wear at OCP	4.91	1.07E-05	0.6722	1211
Sample 1 EIS after wear at OCP	5.28	1.39E-05	0.5313	929
Sample 2 EIS before wear at OCP	5.87	4.67E-06	0.8351	$2.42 \times 10^6$
Sample 2 EIS after wear at OCP	6.32	4.48E-06	0.8586	$2.39 \times 10^6$
Sample 2 EIS after wear at anodic potential	4.26	2.30E-05	0.7099	8672

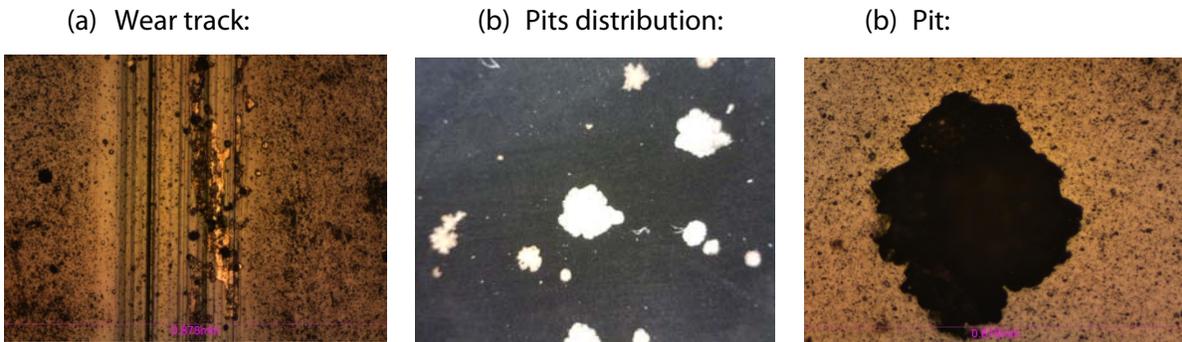
**Table 3: Best-fit values of EIS spectra before and after tribocorrosion tests.**

### Tribocorrosion tests at Anodic Potential

In order to further demonstrate the contribution of corrosion in tribocorrosion process, the tribocorrosion tests were performed at an anodic potential on Sample 2. At an anodic potential (+0.5 V vs. OCP), the rate of corrosion process is increased by accelerated electron removal and metal dissolution. The evolution of the current was monitored before, during, and after the wear test as shown in Fig. 7a, and the EIS before and after the tribocorrosion test at anodic potential is compared in Fig. 7b. It can be observed that the anodic current progressively increases from ~ 0 to ~0.08 A throughout the test, indicating an accelerated corrosion process due to pitting corrosion attack. This leads to substantial reduction of the  $R_{ct}$  from  $\sim 2.4 \times 10^6 \Omega$  to 8672  $\Omega$  for Sample 2. As shown in Fig. 8, the synergistic effect of corrosion and wear leads to failure of the coating in the wear track. Localized corrosion took place at anodic potential during the test, resulting in the formation of equally distributed pits of different sizes over the surface.



**Fig. 7: Evolution of the anodic current and EIS on Sample 2 in the anodic wear test.**



**Fig. 8: Sample 2 after the anodic wear test.**

## CONCLUSION

Nanovea Tribometer provides well-controlled quantifiable and reliable tribocorrosion assessment of the protective DLC coatings. Moreover, the in-situ COF, potential and current measurements allow users to correlate different stages of wear process to improve fundamental understanding of the wear/corrosion mechanism. EIS analysis provides non-destructive evaluation of the corrosion resistance of the coatings.

Based on the comprehensive tribocorrosion analysis in this study, we show that the DLC acts as an excellent wear protective coating to the steel substrate when corrosion is not involved. However, the synergistic effect of corrosion and wear can lead to coating failure and pitting attack to the substrate. This tribocorrosion assessment allows us to evaluate and select the best coating-substrate system to be used in environments that involve wear and corrosion attacks at the same time.

Nanovea Tribometer offers precise and repeatable wear and friction testing using ISO and ASTM compliant rotative and linear modes, with optional high temperature wear, lubrication and tribocorrosion modules available in one pre-integrated system. Optional 3D non-contact profiler is available for high resolution 3D imaging of wear track in addition to other surface measurements such as roughness and pitting analysis.

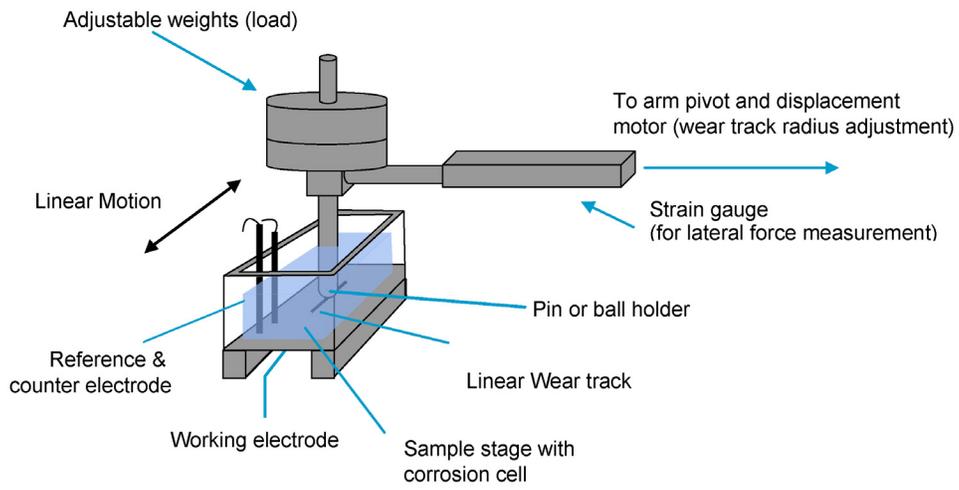
Learn more about the [Nanovea Tribometer](#) or [Lab Services](#)

## REFERENCES

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- [2] D. Landolt, S. Mischler, M. Stemp, Electrochimica Acta 46 (2001) 3913-3929.
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## APPENDIX: TEST PRINCIPLE

As shown in the schematic in Fig. 9, the tribocorrosion cup is fixed on a reciprocating stage. The conventional three electrode setup up is used to monitor the change of voltage and current before, during and after the wear process. The sample is mounted against an O-ring (2.5 cm dia.) with a surface area of 4.91 cm<sup>2</sup> exposed to the electrolyte. The sample serving as the working electrode is connected from the back. A known force is applied on a pin, or ball, in contact with the sample surface to create the wear. The evolutions of coefficient of friction, COF, and open circuit potential, OCP, are recorded in situ. The volume lost allows calculating the wear rate of the material. Since the action performed on all samples is identical, the wear rate can be used as a quantitative comparative value for wear resistance.



**Fig. 9: Schematic of the tribocorrosion test.**