Introduction to the Scanning Droplet Cell (VSC-SDC)

Application Note: 2023/08

The Scanning Droplet Cell (SDC) is an electrochemical technique utilizing a microcell scanning probe. Within the SDC setup, an electrolyte droplet forms between the sample and the capillary in the SDC head, creating an electrochemical cell. The sample itself acts as the working electrode, and the reference and counter electrodes are situated within the SDC head, establishing a two- or three-electrode cell on the scale of the droplet in contact with the sample.

While conventional electrochemical and impedance methods can be performed within the droplet, SDC is unique in its capability to map the electrochemical properties of the sample with a set dc bias or ac frequency, as illustrated in Fig. 1.

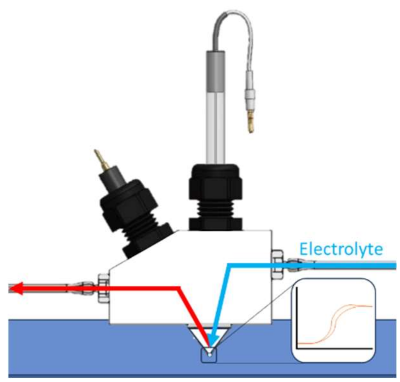

Figure 1. Schematic of the VSC-SDC. The sample acts as the working electrode, and the refence electrode and counter electrode are situated within the SDC head. The electrochemical measurements are conducted in the droplet between the sample and the SDC head.

SDC offers the advantage of providing a direct and localized measurement of the sample. This straightforward interpretation of measurements is possible because fundamental bulk electrochemical principles can be applied directly. A unique feature of SDC is its ability to expose only a small, droplet-sized area of the sample to the electrolyte during each measurement point. This contrasts with most other scanning probe electrochemistry techniques, which require the entire region of interest to be immersed in the electrolyte for measurement.

This feature makes SDC particularly appealing for in situ measurements of samples that could be adversely affected by extended exposure times to the measurement electrolyte. For instance, it proves useful in corrosion studies. By enabling localized and direct electrochemical measurements, SDC has found applications in various fields, including catalysis [1, 2], corrosion [3], materials [4, 5], and energy [6, 7].

The VSC-SDC module is equipped with a flow head configuration, enabling the continuous renewal of electrolyte during measurements. The flow head incorporates a tip opening of 500 µm.

Experimental Procedure

In all measurements, a 100 mM KCl aqueous solution served as the electrolyte. The working electrode for each case was the sample itself, and a single Pt wire functioned as a combined reference and counter electrode (RE/CE). Three distinct samples were subjected to measurement:

(1) The standard 5mm dia. gold disk sample.
(2) The standard Fe/Zn Scanning Kelvin Probe (SKP) sample.
(3) The trimetallic Cu/Zn/Fe sample.

Similar to the standard samples, the trimetallic sample was embedded in resin and polished flat. An electrical contact was established to the backside to allow its role as a working electrode. All samples were polished on wet P4000 silicon carbide paper and followed by rinsing with deionized water prior to each measurement.

Two distinct measurement methods were implemented: the potentiostatic mode and the open circuit mode. For demonstration purposes, the standard 5mm gold disk sample was utilized in the potentiostatic mode. In this mode, a potential of 350 mV was applied to the sample, and the resulting current was measured. On the other hand, the open circuit mode was employed for the standard SKP sample and the trimetallic Cu/Zn/Fe sample. In this mode, the open circuit potential (OCP) was measured at each data point.

All samples were securely positioned within the VersaSCAN L-Cell, and for enhanced access to the SDC head and improved visibility of the droplet, the glass body was removed. To ensure precise alignment, a circular spirit level was employed to level the sample. This procedure consistently yielded a sufficiently level sample surface across the intended scan area, thereby ensuring continuous contact between the droplet and the sample throughout the measurement.

Throughout all measurements, a uniform scan rate of 50 µm/s was employed. The proximity of the SDC head to the sample surface, ensuring it was within 50 µm or less, was meticulously monitored using VersaCAM. A controlled flow of approximately 1 mL/min was maintained using the pump, where the electrolyte to and from the SDC Head are balanced to confine the droplet to the immediate vicinity beneath the tip. It is important to note that the eventual size of the droplet is contingent upon the distance between the SDC Head and the sample, the specific sample and electrolyte combination being applied.

All measurements and corresponding graphs in this application note were carried out using the VersaSCAN software, and no additional post-processing was applied.

Results

Figure 3 illustrates the gold disk sample (A) and the results derived from the mapping procedure, presented as a top view (B) and a side view (C). This mapping was carried out using the potentiostatic mode. In the scope of this investigation, a quarter of the sample underwent mapping. It's worth highlighting that the boundary of the gold disk became remarkably distinct, and concurrently, a substantial surge in current was observed upon the micro electrochemical cell formation with the gold disk surface. Noteworthy as well are the regions exhibiting diminished current, which correspond to areas on the gold disk's surface displaying scratches.

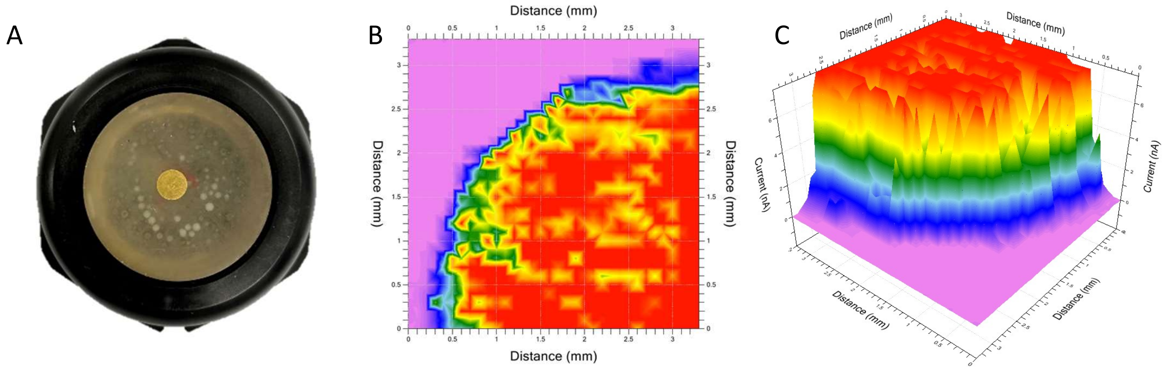

Figure 3. The standard 5mm diameter gold disk sample (A) and the results obtained through the potentiostatic mapping process, depicted in a top view (B) and a side view (C)

The standard SKP (Scanning Kelvin Probe) sample is illustrated in Figure 4A, which was measured with open circuit mode. The sample under examination consists of a plate made of zinc (Zn) coated iron (Fe), where the underlying Fe is exposed through acid etching. Notably, the distribution of the Zn coating on this specific sample is uneven, as indicated by darker spots dispersed across the surface.

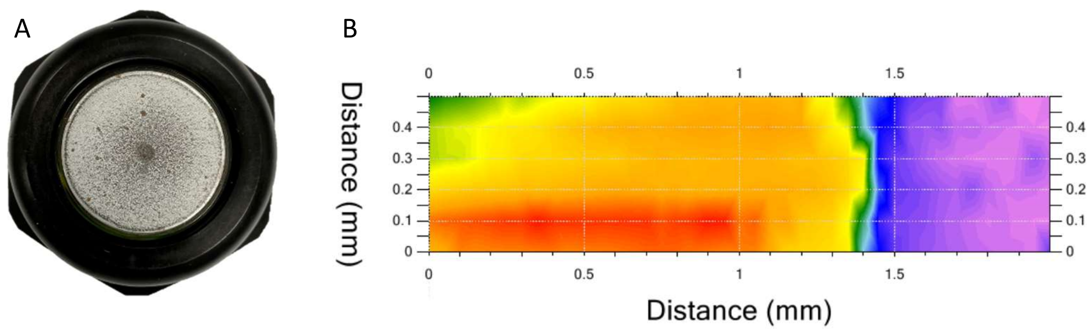

Figure 4. The standard Fe/Zn Scanning Kelvin Probe (SKP) sample (A) and the open circuit mapping results (B).

In Figure 4B, the mapping results with open circuit potential (OCP) measurement are presented. This measurement was conducted by traversing the sample from the region composed of Fe to the area coated with Zn. The data reveal a noteworthy observation: the corrosion potential varies in the sequence Zn < Fe. Furthermore, some irregularities in the OCP values between the Fe region and the Zn-coated area are visually evident. This suggests that there are variations in the electrochemical behavior and corrosion tendencies between these two regions of the sample.

Fig. 5 shows the trimetallic Cu/Zn/Fe sample(A) and its OCP mapping result. Intentional alignment was executed to ensure that while scanning in the positive X direction, the probing head successively measured the OCP of Copper (Cu), Zinc (Zn), and Iron (Fe).

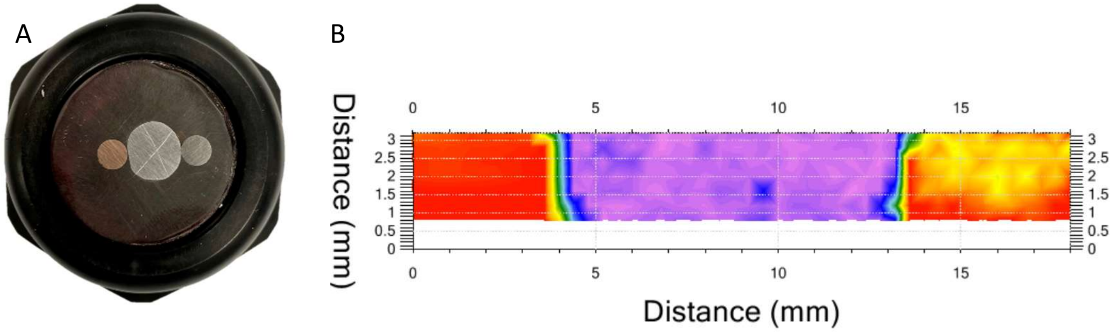

Figure 5. The trimetallic Cu/Zn/Fe sample (A) and the open circuit mapping results (B).

The OCP mapping results are visualized in Figure 5B. It is clear from the map that the corrosion potential adheres to the expected sequence: Zn < Fe < Cu. This observation is consistent with the typical electrochemical behavior of these metals, where zinc corrodes more readily than iron, and copper displays the highest resistance to corrosion among the three.

Conclusion

Three samples have been employed to showcase the application of VSC-SDC. The utilization of SDC measurements has enabled the real-time evaluation of localized electrochemical attributes, including current and open circuit potential, within these samples. This indeed represents a distinct advantage compared to other scanning probe electrochemical techniques, which might rely on indirect measurements, are carried out outside the experimental setup (ex situ) or necessitate calibration to ascertain the outcomes.

This application note showed how the VersaSCAN system with VSC-SDC module performs potentiostatic and open circuit tests on three distinct samples. Depending on your specific sample and requirements for the application, we can provide you with the experimental and instrumentational information to meet the requirements for your measurements. We will be happy to discuss your needs and recommend the most suitable instrument.

Reference

[1] J. Li, H. S. Stei, K. Sliozberg , J. Li, Y. Li, G. Sertic, E. Scanley, A. Ludwig, J. Schroers, W. Schuhmann, A. D. Taylor, ***J. Mater. Chem. A,*** 2017,**5**, 67-72.

[2] B. H. Meekins, A. B. Thompson, V. Gopal, B. A. Tavakoli Mehrabadi, M. C. Elvington, P. Ganesan, T. A. NewhouseIllige, A. W. Shepard, L. E. Scipioni, J. A. Greer, J. C. Weiss, J. W. Weidner, H. R. Colón-Mercado, ***Int. J. Hydrog. Energy,*** 2020, **45,** 1940-1947.

[3] E.B. Tetteh, L. Banko, O. A. Krysiak, T. Löffler, B. Xiao, S. Varhade, S. Schumacher, A Savan, C. Andronescu, A Ludwig, W. Schuhmann, ***Electrochem. Sci. Adv.,*** 2022, **2,** e2100105.

[4] B. DeCost, H. Joress, S. Sarker, A. Mehta, J. Hattrick-Simpers, ***JOM***, 2022, **74**, 2941–2950.

[5] M. Fan, K. Sliozberg, F. La Mantia, N. Miyashita, M. Hagymasi, C. Schnitter, A. Ludwig, W. Schuhmann, ***ChemElectroChem,*** 2014, **1,** 903 – 908.
[6] S. Dieckhöfer, W. Schuhmann, E. Ventosa, ***ChemElectroChem***, 2021, **8,** 3143–3149.
[7] J. P. Kollender, J. Gasiorowski, N. S. Sariciftci, A. I. Mardare, A. W. Hassel, ***Sci. Technol. Adv. Mater.,*** 2014, **15,** 054201

Summary – This application note showed how the VersaSCAN system with VSC-SDC module performs potentiostatic and open circuit tests on three distinct samples.

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