Application Note

Scanning Electrochemical Microscopy (SECM) for Insights on Water-Splitting Electrocatalysts

Application Note: 2024

Introduction

Scanning Electrochemical Microscopy (SECM) is a versatile analytical technique that combines high spatial resolution with electrochemical measurements, enabling detailed investigation of electrochemical processes at interfaces and on surfaces. This application note outlines the principles, advantages, and case studies on the SECM technique using the AMETEK Princeton Applied Research systems.

Principles of SECM

SECM operates by scanning a microelectrode probe over a sample surface immersed in an electrolyte solution. The probe acts as a working electrode in an electrochemical cell and is capable of both generating and detecting electrochemical signals. By controlling the potential of the probe and monitoring the current, SECM can map the local electrochemical reactivity of the sample surface.

Key components and principles include:

- Microelectrode Probe: A fine electrode with a well-defined geometry, typically made of noble metals (e.g., platinum, gold) or carbon materials, with a radius in the micrometer range.
- Distance Control: Precise control of the probe's distance from the sample surface is crucial for accurate measurements, typically achieved through feedback mechanisms.
- Current Measurement: The faradaic current is measured as a function of the probe's position, providing information about the local chemical environment.

Advantages of AMETEK Princeton Applied Research SECM System

- High Sensitivity and Accuracy: The potentiostats/galvanostats offer precise control and measurement capabilities.
- Versatility: Compatible with various electrode materials and configurations, allowing adaptation to diverse research needs.
- User-Friendly Software: The control software is designed for intuitive operation and robust data analysis, enabling researchers to focus on their experiments.

Case #1:

In a recent study, Levinas et al.[(1)] designed a femtosecond (fs) laser-ablated copper surface as a substrate for MoS_2-based hydrogen evolution reaction (HER) electrocatalyst for water-splitting in acidic media, typically replicating the PEM electrolysis conditions. The AMETEK SECM system equipped with a Versa STAT 3 and Versa STAT 3F potentiostat, was employed to study the surface electrochemical behavior and spatial distribution of the HER activity over the laser-ablated samples. The substrate-generation tip-collection (SG/TC) mode was used, where the sample being investigated was used to generate hydrogen, and the tip

©Copyright 2024 AMETEK, Inc. All Rights Reserved

would oxidize the generated products. The electrolyte was 0.5 M H_2SO_4, the probe was a Pt ultramicroelectrode with a 10 µm diameter and the probe-to-sample distance was ~10 µm.

After assembly, an LSV curve was obtained to identify the hydrogen bubbling location and rate (Figure 1). Galvanostatic conditions were found to provide more reliable results. Subsequently, the sample was subjected to current densities from −0.5 to −10 mA/cm², with the potential response recorded. Higher currents resulted in higher overpotentials and quicker steady-state achievement in the fs-Cu/MoS_2 sample. The electrochemical behavior of a 10 µm Pt probe was evaluated by positioning it 10 µm from the surface and holding it at 0 V vs. Ag/AgCl for 50 seconds, followed by applying current to the sample for 200 seconds and then turning it off, providing insight into expected signal characteristics.

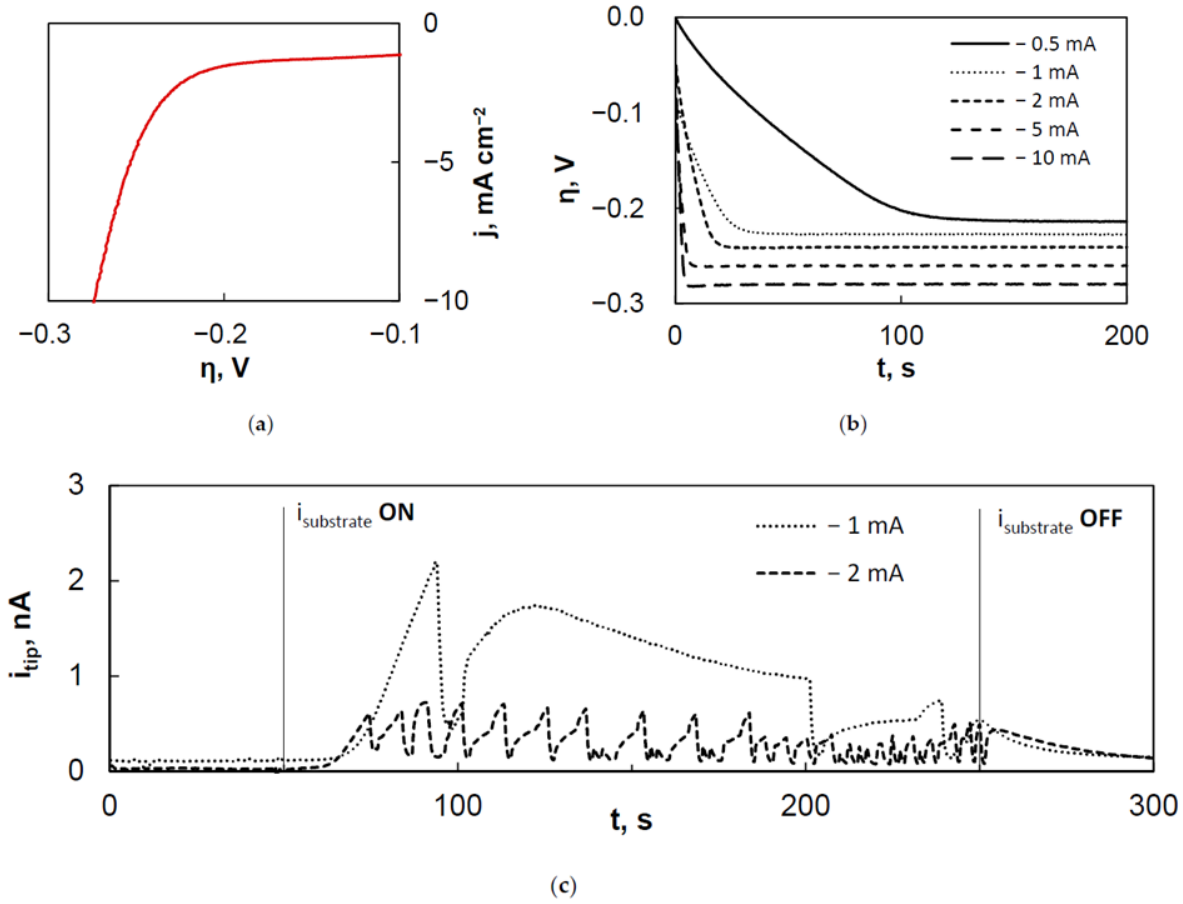


Figure 1. The result of the electrochemical behavior experiments of fs-Cu/MoS_2 in the SECM: (a) LSV curve; (b) settling of the substrate overpotential under different applied currents; (c) the kinetics of the probe response to the substrate generation signal. Reproduced with permission from (1)

The widths of the fs-Cu peaks and pits observed in the SECM mapping (Figure 2) matched well with the profilometric analysis results. The SECM signal was due to the oxidation of products generated by the substrate, reflecting the radial diffusion of these products away from the sample. The close match between some 2D slices (e.g., Y − 40 µm and Y − 60 µm) and the profilometric slice (Figure 2b, dashed line) suggests that HER activity is similar on both pits and peaks.

©Copyright 2024 AMETEK, Inc. All Rights Reserved

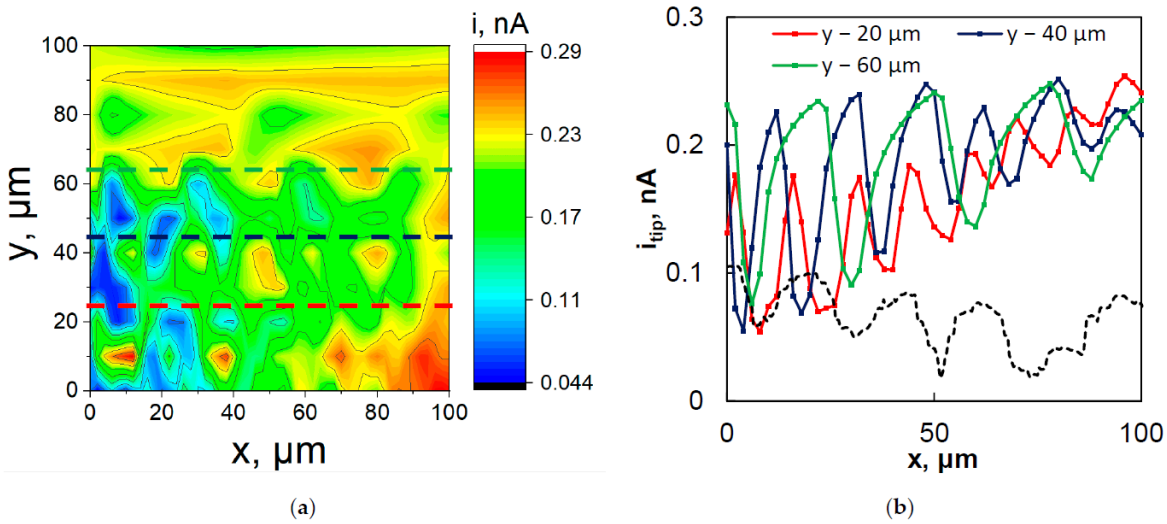


Figure 2. (a) The SECM map and (b) horizontal slices plus profilometry slice (from a different sample, only shown for reference) in the black dashed line of fs-Cu/MoS2. The map was obtained in SG/TC mode. The sample is galvanostatic at -2 mA, tip potentiostatic at 0 V vs. Ag/AgCl. Measured in 0.5 M H_2SO_4, probe scan rate 5 µm s^{-1}, tip diameter 10 µm. X step size 2 µm, Y step size 10 µm. Reproduced with permission from (1)

Case #2:

In another study[2], Ramunas and co-workers developed a WO_3/MoS_x heterostructure bifunctional catalyst for photo/electrochemical overall water-splitting and evaluated their behavior using the SECM system. The mode of operation was substrate-generation/tip collection (SG/TC), where the substrate (WO_3/MoS_x heterostructures) acted as a generator and the 25 µm Pt tip as a collector. Before measurement, the substrates underwent equilibration by applying a −0.3 mA cm^{-2} current for 20 minutes until a stable HER overpotential was achieved. Once conditions were stable, the probe was lowered to 15–25 µm from the substrate using an approach curve method. The probe was then polarized to 0 V (vs. Ag/AgCl) for hydrogen oxidation, and a 2D map was obtained by scanning the probe at 100 µm/s, recording data points at 25 µm intervals.

The SECM mapping data, shown in Figure 3, includes 2D slices and maps of the respective films. For the 2-min-WO_3/MoS_x film, no distinct features were observed, suggesting a smooth surface with minimal MoS_x content, as indicated by SEM and FIB observations. However, minor current bumps were noted around 0.4–0.5 mm and 0.7–0.9 mm, likely due to substrate topography. In contrast, the 5-min-WO_3/MoS_x film showed significant inhomogeneity in HER activity, with several ~0.2 × 0.2 mm islands of increased activity across the 1 × 1 mm map, indicating the presence of active sites influenced by MoS_x and surface topography. The 30-min-WO_3/MoS_x film displayed similar patterns of electrocatalytic activity but with greater variation in measured currents (~0.5 nA compared to 0.1 nA for the 5-min film), suggesting increased surface roughness and MoS_x content, leading to more pronounced local HER activity variations.

©Copyright 2024 AMETEK, Inc. All Rights Reserved

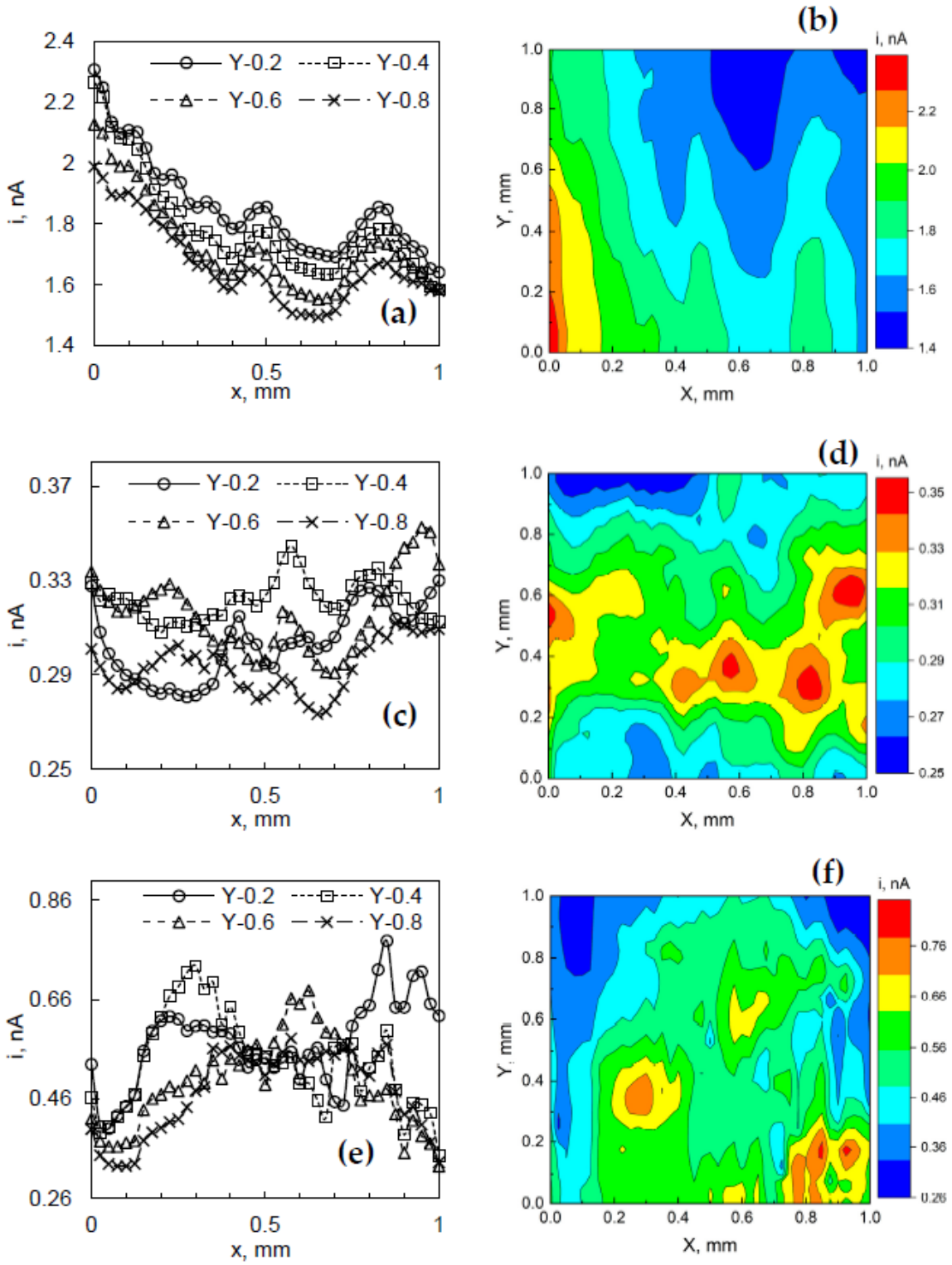


Figure 3. 2D profiles and 2D SECM maps: 2-min-WO_3/MoS_x (a,b); 5-min-WO_3/MoS_x (c,d); 30-min- WO_3/MoS_x (e,f) films, obtained in 0.5 M H2SO4. Probe scan speed 100 µm s^{-1}, data acquisition at 25 µm intervals with a 25 µm diameter probe. Reproduced with permission from (2)

©Copyright 2024 AMETEK, Inc. All Rights Reserved

Conclusion

The SECM systems from AMETEK Princeton Applied Research provide a powerful platform for studying electrochemical phenomena with high spatial resolution and have demonstrated great benefits in the electrocatalysis area. With their advanced instrumentation and versatile applications, these systems are invaluable tools for researchers in academia and industry alike.

References

1. Levinas, R.; Grigucevičienė, A.; Kubilius, T.; Matijošius, A.; Tamašauskaitė-Tamašiūnaitė, L.; Cesiulis, H.; Norkus, E. Femtosecond Laser-Ablated Copper Surface as a Substrate for a MoS_2-Based Hydrogen Evolution Reaction Electrocatalyst. *Materials* 2022, *15*, 3926. https://doi.org/10.3390/ma15113926
2. Levinas, R.; Tsyntsaru, N.; Cesiulis, H.; Viter, R.; Grundsteins, K.; Tamašauskaitė-Tamašiūnaitė, L.; Norkus, E. Electrochemical Synthesis of a WO3/MoSx Heterostructured Bifunctional Catalyst for Efficient Overall Water Splitting. Coatings 2023, 13, 673. https://doi.org/10.3390/coatings13040673

Note: For further information or support, contact us at www.ameteksi.com

©Copyright 2024 AMETEK, Inc. All Rights Reserved