Supporting Information

Controlling Surface Contact, Oxygen Transport and Pitting of Surface Oxide via Single-Channel Scanning Electrochemical Cell Microscopy

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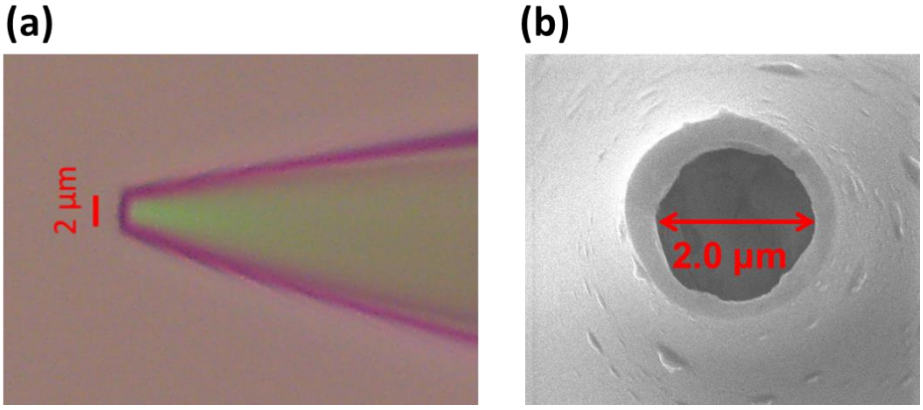

Figure S1. (a) Optical microscopic and (b) SEM images of the micropipette.

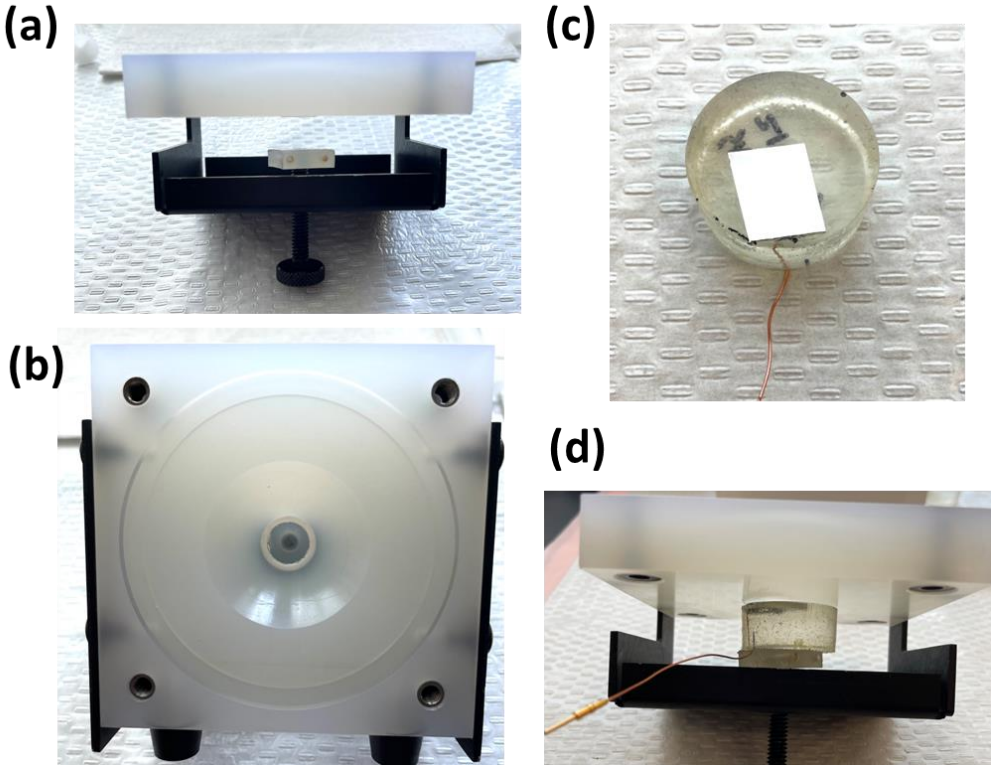

Figure S2. (a) Side view and (b) top view of the cell holder for Al alloy working electrode. (c) An Al alloy piece embedded in the resin. (d) The Al alloy sample was fixed in the cell holder.

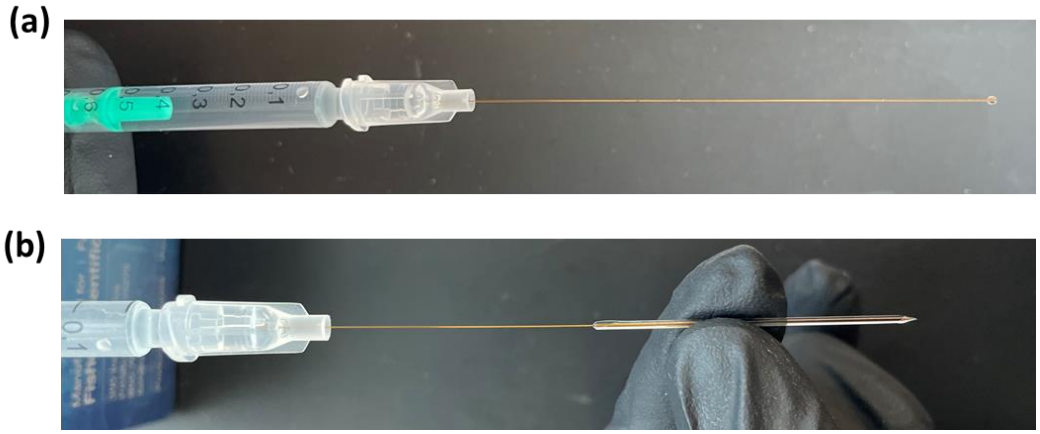

Figure S3. (a) Microneedle filled with electrolyte solution. (b) Micropipette was filled with electrolyte solution.

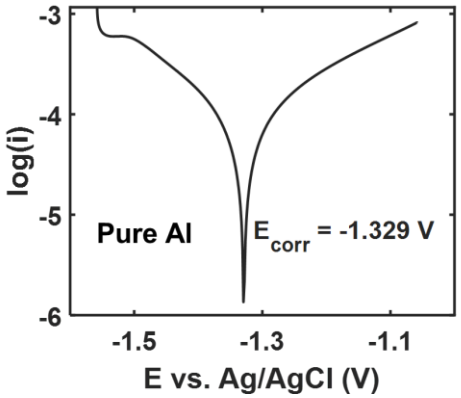

Figure S4. Bulk PDP measurement of pure Al at the scan rate of 0.167 mV/s. The potential was referred to SCE during the experiment. To be consistent with the potentials in SECCM, the potential was converted to be referred to the Ag/AgCl wire electrode in a 3.5 wt% NaCl solution. The surface area of Al exposed to the 3.5 wt% NaCl electrolyte was 1 cm^2.

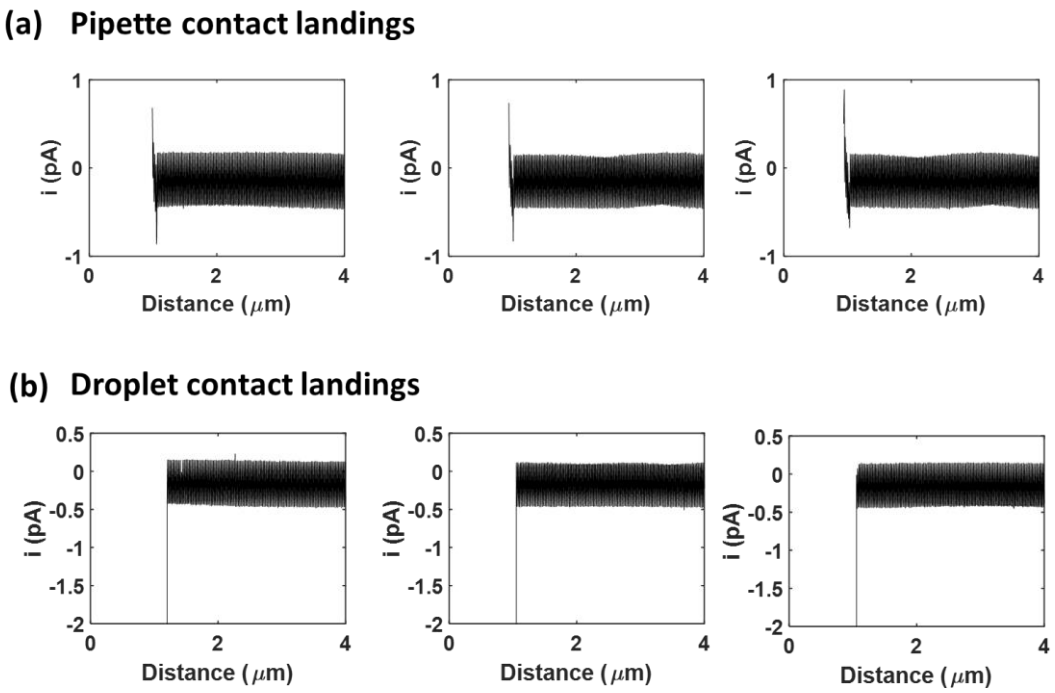

Figure S5. Currents recorded during the 2 µm diameter micropipette approach to the surface of aluminum alloy AA7075-T73 at a cathodic approach potential of (a) -1.5 V and (b) -2.5 V vs. Ag/AgCl.

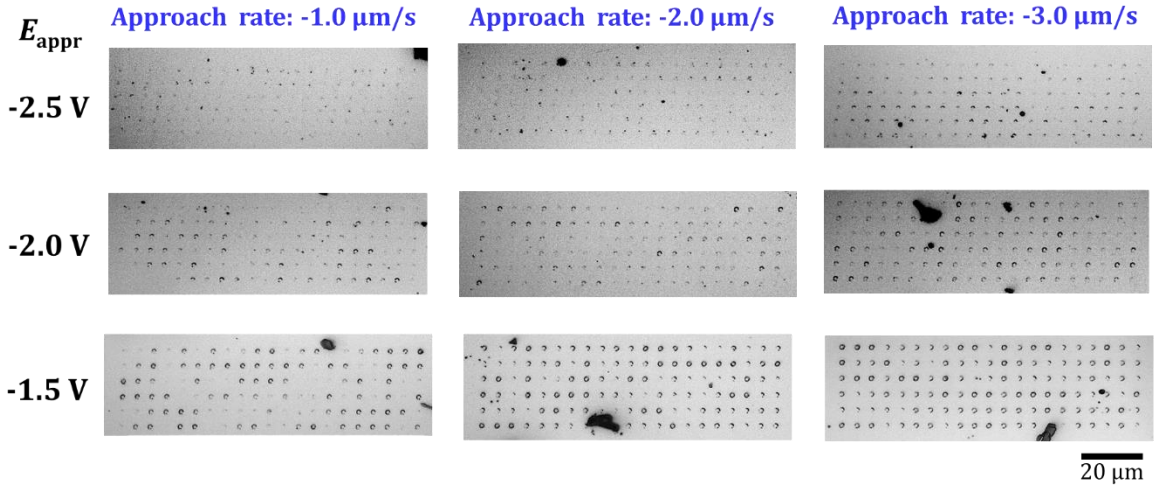

Figure S6. Optical microscopic images of landings on the Al alloy AA7075-T73 after oil-immersed SECCM experiments using 2 µm diameter pipettes filled with the 3.5 wt% NaCl electrolyte. The micropipettes were approached to the substrate at rates of -1, -2, -3 µm/s with E_{appr} of -2.5, -2.0, -3.0 V vs. Ag/AgCl, respectively. The small dots were left by droplet contact landings. The circles are the indentations of pipette contact landings.

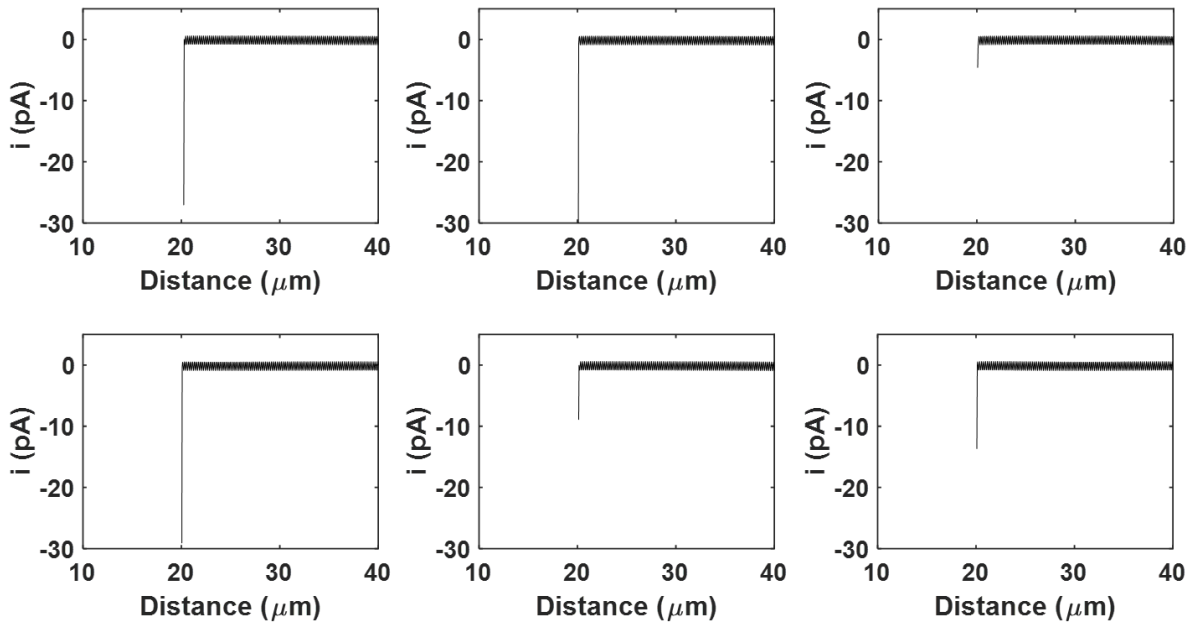

Figure S7. Currents recorded during the 10 µm diameter micropipette approach to the surface of aluminum alloy AA7075-T73 at a cathodic approach potential of -1.5 V. Negative trigger currents (i_{trig}) were produced as a result of droplet contact landings.

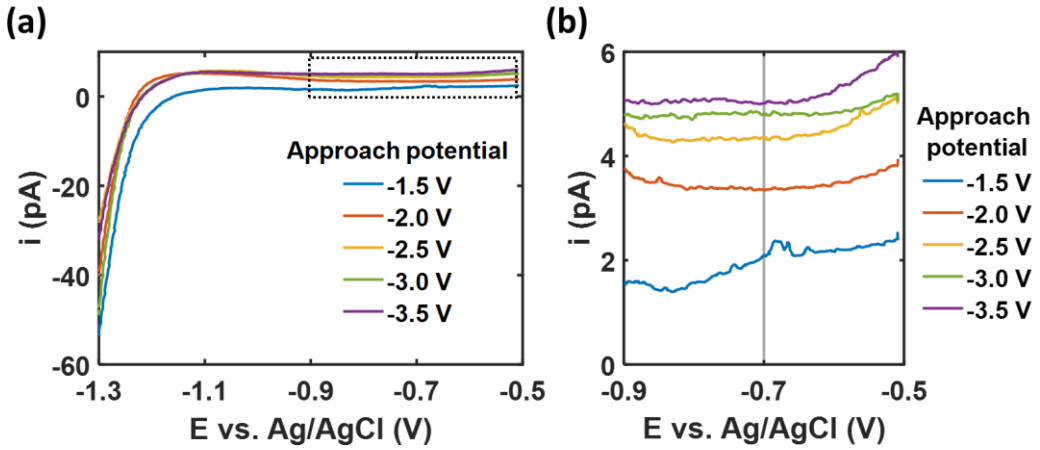

Figure S8. (a) PDP curves at the landing locations with different approach potentials applied. (b) Anodic currents at -0.7 V vs. Ag/AgCl were extracted.

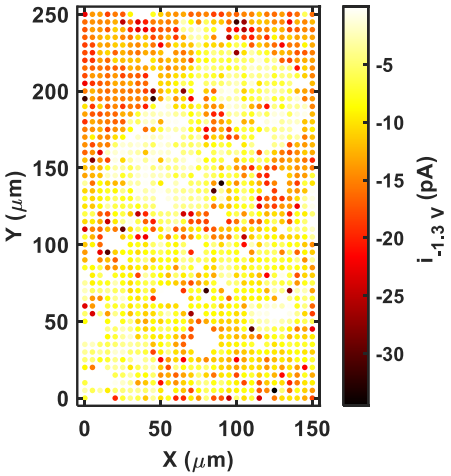

Figure S9. Cathodic currents at -1.3 V vs. Ag/AgCl were extracted from an oil-immersed SECCM experiment performed on an Al alloy. At each droplet landing location, a potentiodynamic polarization was conducted from -1.4 to -0.3 V vs. Ag/AgCl at a scan rate of 100 mV/s. The map implies a correlation between cathodic corrosion currents and surface grain orientations.