Supplemental Information

5.1 Basics of Shear-Force Imaging

A schematic showing the configuration of an electrode tip with attached piezoelectric plates and sample approach curve is shown in Figure 6.

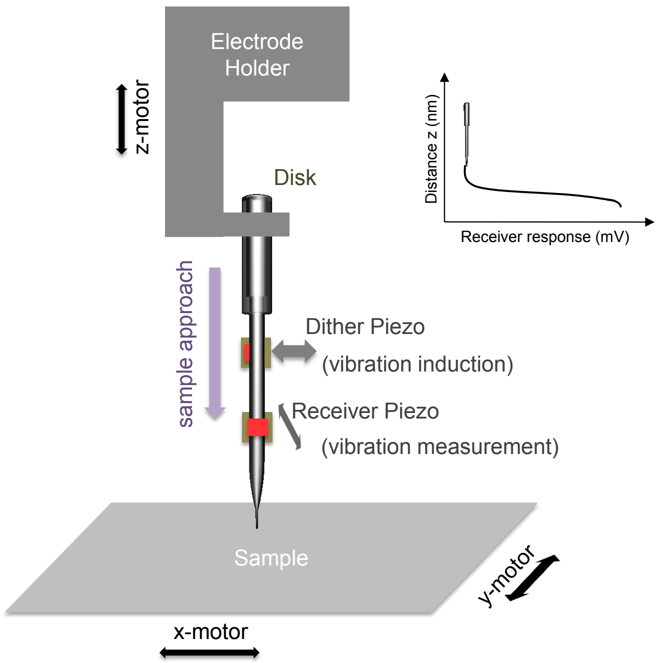

Fig. 6 Schematic of a SECM-SF measurement configuration in the vicinity of a substrate with (inset) a sample approach curve

For shear force imaging techniques, piezoelectric plates (HEKA Elektronik Dr. Schulze GmbH) were connected to a nanoelectrode on the quartz capillary, with a 1 cm spacing and approximately 90° rotation between them. The Pt-nanoelectrode was positioned in the x,y plane directly above the PPy(DBS) membrane with a joystick, and brought into contact with the sample by moving in the -z direction until an abrupt change in the shear force signal was observed. This signal indicates contact with the sample surface.

A list of specific experimental steps to perform a dynamic characterization of faradaic materials is as follows:

- Mount the electrode to z-stage
- Mount the sample to x,y-stage, add electrolytic solution and apply an oxidation signal to the sample (ring electrode)
- Use zz-motors to position electrode tip into solution and x,y-motors to position the electrode tip above the sample
- Use "Tip Down" procedure with current regulation (10%) to approach the sample until the electrode is in the immediate vicinity
- Use the "2D Scan" with z-piezo motor selected to approach the sample at a rate of -0.05 μm/sec while simultaneously monitoring current and shear force signals
- Upon reaching the "Contact Condition" (characterized by a discontinuous current response or shear response) manually "Stop" the "2D Scan"
- Perform "Shear Force Spectra" procedure with the electrode maintained at "Contact" position
- Set origin in ElProScan: Motors window
- Perform the "Distance Calibration" procedure for with a 2.5 μm distance with a 3 nm step size
- Perform the "Shear Force Spectra" procedure with the electrode maintained at the "Non-Contact" position
- Overlay the two shear force spectra plots to select an operational frequency
- Perform a "Distance Calibration" procedure to ensure a monophasic approach curve - otherwise, select a new operational frequency and repeat until a monophasic approach curve is found
- Open the shear-force tracking protocol window, input a set value, slope, upper and lower datums based on the approach curve (see Figure 1 for specification)
- Move the electrode in the z-position to the sense length
- Run the shear-force tracking protocol while monitoring to ensure operation does not move out of the maximum and minimum SF limits
- Remove the electrode from solution by moving zz-motors in the positive direction before turning off the software

It is noted that the maximum frequency of measurements taken during operation was roughly 5 samples/second. This slow measurement response time is due to current limitations in the POTMASTER software and is expected to be improved by integrating the external control protocol onto the real time measurement board. The addition of the 10x gain in the SF-signal used for dynamic tracking was a critical element, as shear-force tracking requires monophasic approach curves with a significant linear response region for accurate system response (shear force regulation) to an input (membrane z-displacement). Based on a more rigid measuring criteria, several approach curves were taken at various frequencies before a suitable operational frequency was selected. The 10x gain allowed for a greater number of frequencies to be tested due to the amplification of the difference between contact and non-contact boundary conditions, thus increasing the odds of attaining an “ideal" approach curve.

5.2 POTMASTER Code for Dynamic Tracking of Surfaces

The pseudocode for this protocol using a HEKA ElProScan1 unit with POTMASTER software is as follows:

1. A new group is created in the protocol editor to store relevant data
2. Input SET value (SF in mV) to maintain
3. Input SLOPE value (SF-amp/z, in mV/nm)
4. Establish maximum and minimum limit for regulation parameter
5. Establish z-motion commands (2 move mode, 0; move relative)
6. Run Analysis “SF-Z-Track”, output to notebook the following values:
   (a) Timer (set initial timer to 0)
   (b) Z-position (ElProScan Function Trace 1)
   (c) Slope
   (d) Set Value
7. Define outer loop (OL) - repeat tracking program XX number of times

- **OL1:** Input most recent parameters from analysis “SF-Z-Track” from notebook
- **OL2:** Run Pulse Generator File “zTrack”
  1. Input Potential (V)
  2. Output Potential, Current for Ring,Disk (V,I)
  3. Define Segment: Stored constants
  4. Define number of sweeps
  5. Define duration of sweep
- **OL3:** Run conditional statement (if,then) tracking timer until initial step input (reduction) and until final step (oxidation)
- **OL4:** Request current SF amplitude from notebook, check against defined limits (if out of limit, break protocol)
- **OL5:** Decide where to move z-piezo:
  1. Check slope sign and compare current SF against SET
  2. If positive, set position as (SET-current SF)/(Slope), copy to “2 movemode”
  3. If negative, set position as (current SF-SET)/(Slope), copy to “2 movemode”
- **OL6:** Output parameters to analysis “SF-Z-Track” notebook
- **OL7:** End OL, increment counter towards XX number of OL repeat segments

An image of the shear-force tracking protocol as used in POTMASTER software is given as Figure 7. This was created using the ”Protocol Editor” and implemented using the Analysis window.

```
 1:  File: NewGroup
 2:  SetOsci: Timer,
   ;-- set parameters --
   ;- value 11 is the SET value which we try to keep
 #:  Value: Value-11 =  0.0000
   ;- value 12 is the SLOPE (e.g. SF-ampl / z)
 #:  Value: Value-12 =  0.0000
   ;- value 13 is the reulation parameter, e.g. SF-ampl.
   ;- value 14 is the relative movement in z
   ;- value 15 is the maximum limit for regulation parameter
   ;- value 16 is the minimum limit for regulation parameter
   ;if out of this limit, regulation stops, LOSS OF TRACK
   ;-- main loop --
14:  Command: "2  MoveMode       0; Move Rel."
   ;-- make sure the correct analysis method is selected --
16:  Invalid
17:  Analysis: "SF-Z-Track"
18:  REPEAT: 5 x 0.000s
19:     REPEAT: sweeps 0.000s
20:        Sweep: "zTrack"
21:        IF: RepeatCount =  50.000
22:           Amplifier: Ampl-2
23:           Amplifier: E-init= -800.00mV
24:        ELSIF: RepeatCount =  150.00
25:           Amplifier: E-init=  0.0000V
26:        END_IF
   ;-- adjust z position --
   ;-- ask for SF amplitude --
29:        Value: Value-13 = "4 SF_amplitude"
30:        Value: User_1 =  Value-13
   ;-- check for limits
32:        IF: Value-13 > Value-15
33:           WriteValue: Text, LF, "LOSST TRACK, out of upper limit", ""
34:           BREAK: protocol
35:        ELSIF: Value-13 < Value-16
36:           WriteValue: Text, LF, "LOSST TRACK, out of lower limit", ""
37:           BREAK: protocol
38:        END_IF
   ;-- decide where to move --
40:        IF: Value-12 >  0.0000
   ;-- SLOPE positive --
42:           Value: Value-14 = (v[11]-v[13])/v[12]*1e6, copy to "2 PiezoMove"
43:        ELSIF: Value-12 <  0.0000
   ;-- SLOPE negative --
45:           Value: Value-14 = (v[11]-v[13])/v[12]*1e6, copy to "2 PiezoMove"
46:        ELSE
47:        END_IF
48:     END_REPEAT
49:  END_REPEAT
```

Fig. 7 An image of the shear-force tracking protocol as used in the POTMASTER software.

5.3 Error Rectification for Shear-Force Imaging Techniques

The basis for dynamically tracking a surface via shear-force imaging techniques was to maintain the shear force at a constant value. As the system was perturbed by external inputs (substrate movement in the z-direction) or noise (environmental vibrations, etc), deviations in the shear force caused errors in the z-position. The magnitude of this error can be seen in Figure 8(a), in which the shear force for the 0.6 $C.cm^{-2}$ is displayed over the entire experimental range. In this instance, the input values for maximum shear value, minimum shear value, and slope were 347 mV, 280 mV, and 1.44 mV/nm, respectively.

Since the temporal resolution for the tracking system was low (roughly 5 Hz), this meant any error in the z-position (due to random external vibrations in the testing area) for one cycle resulted in a large deviation before a correction could be made in the next cycle. This can be visualized by plotting the shear force over time (normalized to distance using the approach curve slope) against the raw z-position for a single reduction cycle, as shown in Figure 8(b). In this figure a qualitative trend between noise in the shear-force and the translation of that noise into the measured z-position is obvious. Therefore, a signal rectification is possible by subtracting the normalized shear-force from the z-position after time syncing the two signals. A plot demonstrating the raw z-position data against the rectified signal and the reduction in noise from 60 nm “spikes" to less than 10 nm oscillations is shown in Figure 8(c).

It is important to note that this rectification process is only required for a measurement system with low sampling resolution. In future experimental configurations, a higher sampling time would remove the large sample noise and create smoother response curves.

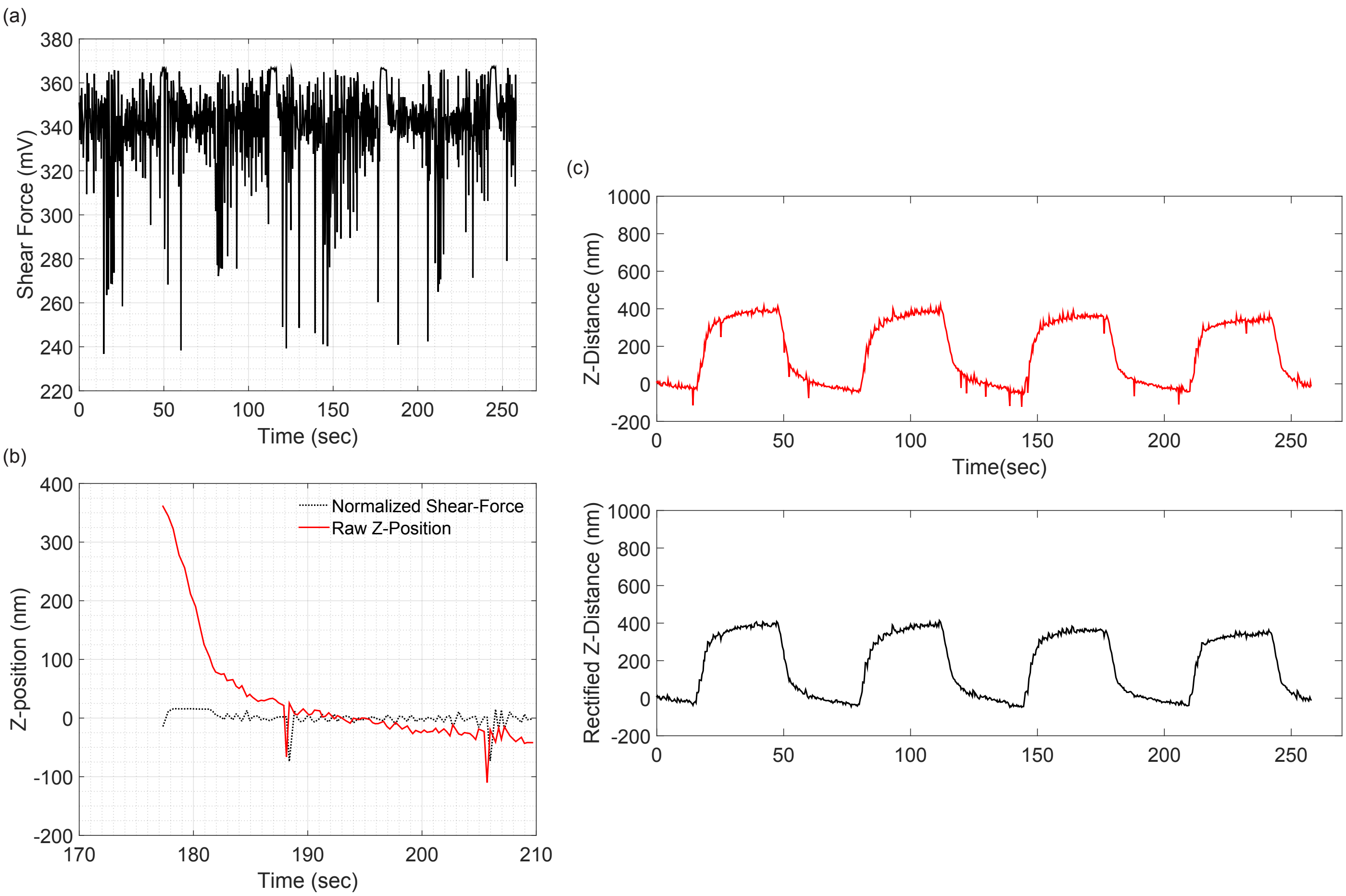

Fig. 8 A plot of (a) the shear-force response vs time during the shear-force tracking process for a 0.6 C.cm^{-2} PPy(DBS) membrane (b) the raw z-position data and shear force normalized to position for a single reduction process for a 0.6 C.cm^{-2} PPy(DBS) membrane and (c) the raw z-position data and rectified z-position data for a 0.6 C.cm^{-2} PPy(DBS) membrane