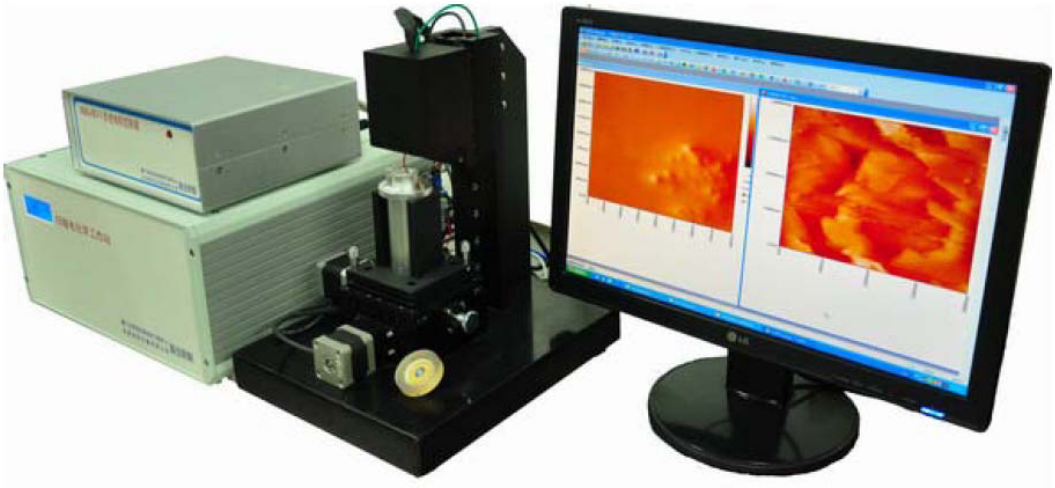
XMU-BY-LG Scanning Electrochemical Workstation

Operation Instruction



Contents

Chapter 1 Preface

1. Announcements

1.1 Grounding

Make sure that the instrument is properly **GROUNDED**, which is the basic requirement of electrical safety. Besides, it also guarantees the anti-interference of the instrument.

1.2 Safety

POWER OFF the controller before any hardwires connection and disconnection.

1.3 Movement of probe

After the probe of the system approaches the sample, the probe can **NOT** be moved and any rotary knob on the probe can **NOT** be adjusted, or the needle will be damaged!

2 Precautions of the scanner

2.1 The core part of the scanner is the piezoelectric ceramic. It is fragile. Please take it gently. Do **NOT** drop it or press it.

2.2 Before using the scanner, please take off the protective lid. After using it, please cover the scanner under the protective lid and put it into dry storage.

2.3 If there is a need to transport the scanner, you must cover up the protective lid and use the vibration-absorptive and cushioning material for packaging.

2.4 The scanner easily gets damaged in the humid environment. If you use the damaged scanner, the circuit of the main controller may get damaged.

2.5 The scanner must be stored in the **DRY** and **ENCLOSED** environment. It is suggested that the user should put the scanner in the dryer or the moisture-proof and enclosed container. Additionally, the user should put a proper amount of silicone moisture-proof materials in the enclosed container.

2.6 After using the scanner, the user **MUST** take the scanner out of the foundation of the scanning platform and then put it in the dry and enclosed environment.

3. Requirements on the working environment

The system requires certain requirements to the working conditions. To ensure the instrument can be used properly and to achieve the ideal function, the user should confirm the following aspects one by one before installing the system:

3.1 General environment demands: the system is a set of fine equipments integrated with mechanics, optics and electronics, suitable for indoor installation. The installation conditions are as follows:

- It is prohibited from getting in contact with rain or other water source so as to avoid electrical failure.
- Do not install the instrument in the acid, alkali or other erosive environment to protect the system from being damaged.
- Do not expose the equipment under the sun for a long time so as to protect the system from aging.
- The core part of the scanning probe microscope is piezoelectric ceramic. The three-dimensional movement can be conducted through controlling the voltage

between each electrode of the scanner. The voltage difference between the electrodes reaches 400V. However, the gap between the electrodes is quite narrow. The insulation capability of the piezoelectric ceramic reduces dramatically after it gets damp. Therefore, the humidity of the working environment should be controlled strictly.

- Environmental temperature: 18 - 25℃
- Environmental humidity: ≤30% (relative humidity)

3.2 Before the system is powered on, the user must ensure that the power supply of the system's installation site is well grounded. A good grounding can not merely enhance the effect of electrical shielding and increase the system's anti-interference ability, but is also a necessity to guarantee the electrical safety. The power of the system is directly supported by municipal AC electricity supply. The voltage designed for the operation of the system is AC220V, allowing a deviation of ±10%. The user must control the deviation within this range. Otherwise, the system should be equipped with steady-voltage power supply.

Notice: If the voltage exceeds the allowed deviation range, the system may fail to work normally. Moreover, it may cause the destruction of the system. In addition, the user should also confirm that there is no frequently-used high-power switch that shares the same power source with the system or the electrical equipment with sudden high-current near the installation site of the system so as to avoid the electromagnetic interference through power line coupling.

3.3 No intense vibration source, the sample of strong sound source scanning probe microscope and relative accuracy of the probe's spatial positioning directly decide its resolution. Vibration and sound source will bring interference, thus reducing the accuracy. As a result, no intense vibration source and strong sound source is the prerequisite of the installation site.

3.4 The probe equipped with the system has good anti-interference capability against sound-, light-, magnet- and vibration. However, in order to achieve the optimal effect, especially when the specific application area of the user puts a high demand on resolution, the equipment should be installed to the anti-vibration equipment which generally adopts optical pneumatic cushion platform or spring anti-vibration mount.

Optical Pneumatic Cushion Platform

Chapter 2 XMU-BY-LG Scanning Electrochemical Workstation

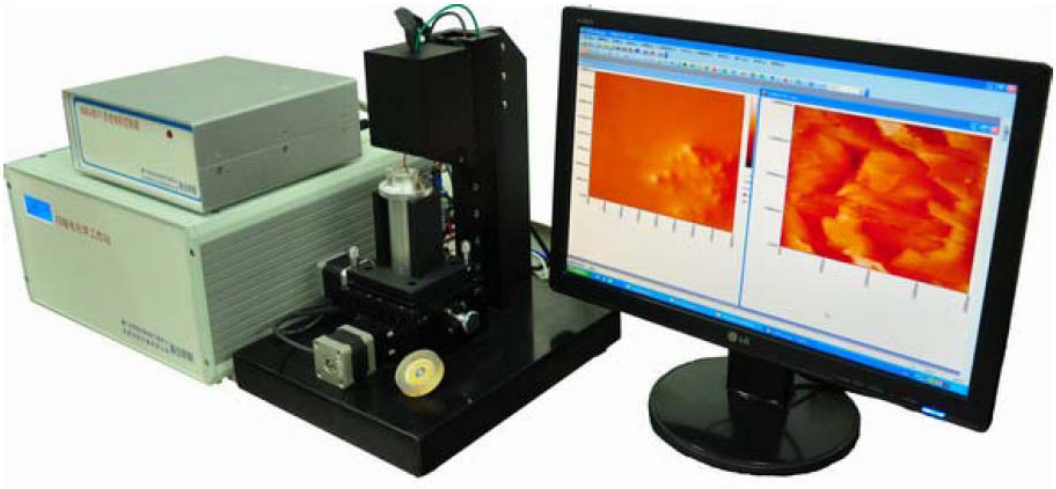
1 Functions of the system

XMU-BY-LG scanning electrochemical workstation can be used for monitoring the *in situ* potential distribution, *in situ* current distribution and STM morphological distribution on the surface of the electrode. Besides, developing and utilizing different kinds of potentiometric ion selective probes can *in situ* test the ion distribution on the surface of the electrode, such as Cl^- and pH.

In addition, the specific target point testing function of XMU-BY-LG scanning electrochemical workstation can automatically position the probing needle in the area which you are interested in, and then track all electrochemical information at this certain area, such as the test of the potential's changes during different periods, the test of the potential's changes with the changes of the distance of X/Y/Z, the test of the material's distribution changes and the test of morphological changes. In addition, we can also carry out the location test in various ways through jointly using the ordinary steady potentiostat.

2. System components

XMU-BY-LG scanning electrochemical workstation is composed of four parts (Picture 2-1): scanning platform (including the scanning probe, foundation of scanning platform, scanner, probing needle mount and probes), controller, machine controller and computer control system.



Picture 2-1 Main composition of XMU-BY-LG scanning electrochemical workstation

2.1 Computer control system

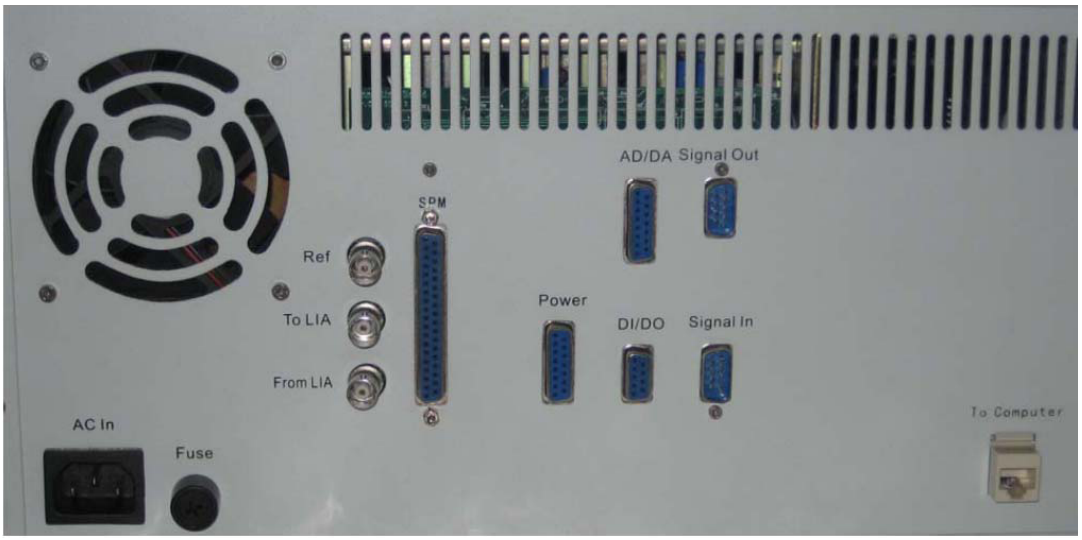
The computer control system includes: computer workstation, computer interface and computer software system.

The computer workstation is a standard microcomputer system. The computer is connected to the controller with Fast Ethernet. The user achieves the control on the equipment in SPM Console on-line control software. The scanning result is output on the computer display screen in real time.

2.2 Controller of XMU-BY-LG scanning electrochemical workstation

The controller is the main electric control system of XMU-BY-LG scanning electrochemical workstation. There is a LCD on the front panel (Picture 2-2), which is used to monitor the state of the system. The back panel (Picture 2-3) reserves multi-channel simulation and digital signal input/output interface, which fully satisfies the user's demand on the application and re-development in the future.

Picture 2-2 Front panel of the controller



The following are the definition of each interface:

AC In	Interface of power supply and the input of AC power supply (AC 220V/50Hz);		
Fuse	Fuse holder (AC 250V/4A);		
SPM	Connection interface of the probe; connected to SPM		
Power*	Output interface of the power supply	Ref#	Refer to signal output
AD/DA*	Simulative signal input/output interface	To LIA#	The needle signal is output to the lock-in amplifier
DI/DO*	Digital signal input/output interface	From LIA#	Input from the lock-in amplifier
Signal Out*	Signal output interface of the instrument		
Signal In*	Signal input interface of the instrument		
Ethernet	Ethernet interface; connect to the control computer through the crossed network line		

Picture 2-3 Back panel of the controller and definitions of each interface

2.3 Scanner of XMU-BY-LG scanning electrochemical workstation

The largest range and resolution of scanning is determined by the scanner chosen by the user (Picture 2-4). The longer scanner can provides a larger scanning range. In general, the scanner with a smaller scanning range can obtains a higher scanning resolution due to the smaller noise impact. The larger scanner can provide a larger scanning range with limited resolution.

Picture 2-4 Scanners of different types

The core part of the scanner is piezoelectric ceramic. According to the added voltage, it can stretch or shorten itself independently on the directions of X, Y and Z. Because of the different physical properties of each piezoelectric ceramic, every scanner has its own specific parameter (extension coefficient and X/Y non-linear parameter). These parameters have been attaches with the scanner.

Notice

1. The scanner is fragile. Please take it gently. Do not drop it or press it.

2 Before using the scanner, please take off the protective lid. After using it, please cover the scanner under the protective lid and put it into good storage.

3 If there is a need to transport the scanner, you must cover up the protective lid and use the vibration-absorptive and cushioning material for packaging.

4 The scanner easily gets damaged in the humid environment. If you use the damaged scanner, the circuit of the main controller may get damaged.

5 The scanner must be stored in the dry and enclosed environment. It is suggested that the user should put the scanner in the dryer or the moisture-proof and enclosed box. Additionally, the user should put a proper amount of silicone moisture-proof materials in the enclosed container.

6 After using the scanner, the user must take the scanner out of the foundation of the searching probe and then put it in the dry and enclosed environment.

3 System interface

The whole system interface can generally be divided into 8 areas as shown in the following (Picture2-5).

A1: Menu bar

A2: System parameters settings

A3: Real-time display window of two-dimensional signal

A4: Window of image buffer area

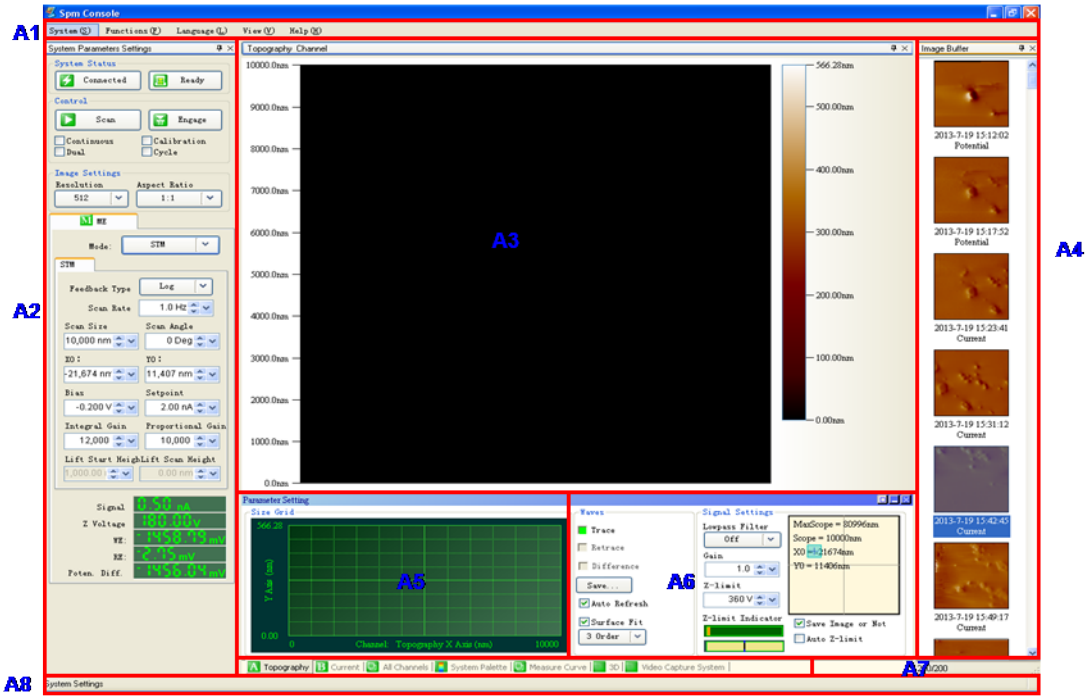
A5: Real-time display window of single line signal

A6: Setting window of signal parameters

A7: Signal switch window

A8: Status bar

Menu bar includes five parts, including system, functions, languages, view and help. System parameters settings windows includes system status, control, image setting, working mode, scanning parameters settings and data display. Real-time display window of two-dimensional signal mainly shows the graphics made with the obtained data. Real-time display window of single signal is mainly used in showing the changes of single-line data in real time. Window of image buffer area is used to store the data graphics temporarily. Setting window of signal parameters is mainly used to adjust the setting of the wave parameters. Signal switch window is used in the switch of different windows. Status bar is use to display the working status of the instrument.



Picture 2-5 Interface of XMU-BY-LG scanning electrochemical workstation system

3.1 Menu directives

3.1.1 System menu

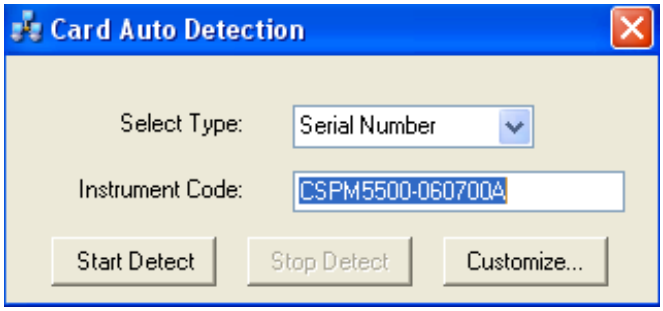
It is mainly used in the system setting of the scanning machine. When using the instrument at first time, we should set the instrument systematically. If there is no significant problem, we do not need to change the systematic setting.

- Net Driver

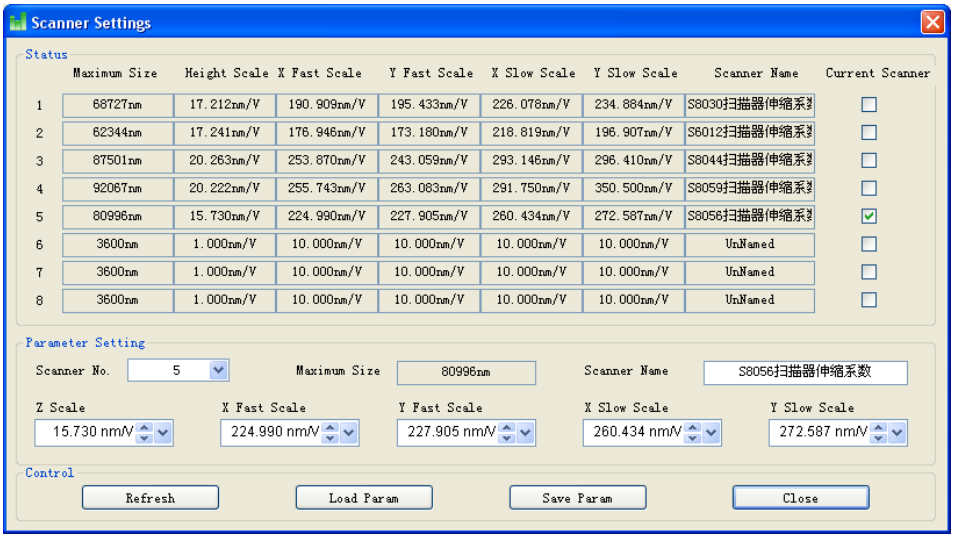
Set the working network of the environment. Usually, we choose Winpcap (recommended). Generally, when we start the software, the instrument will choose and connect the network automatically.

- NICs Setting

It displays the code of the instrument, and then carries out detection. (Picture 2-6)



Picture 2-6 Dialog box of NICs setting



Picture 2-7 Dialog box of setting the scanner

- Scanner Setting

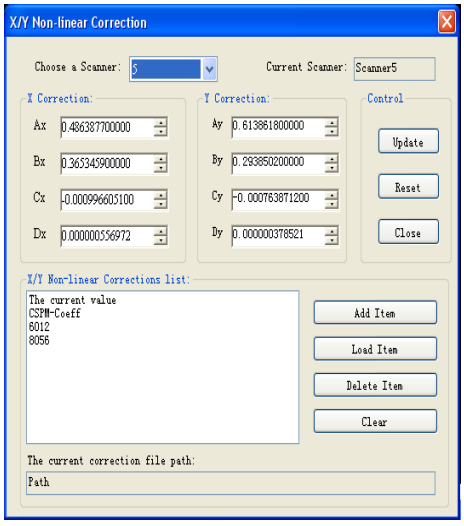
The parameters of the scanner are set in accordance with its type. Generally speaking, different scanners have different scanning parameters. However, one certain type of scanners has fixed scanning parameters. (Picture 2-7)

- X/Y Non-linear Correction

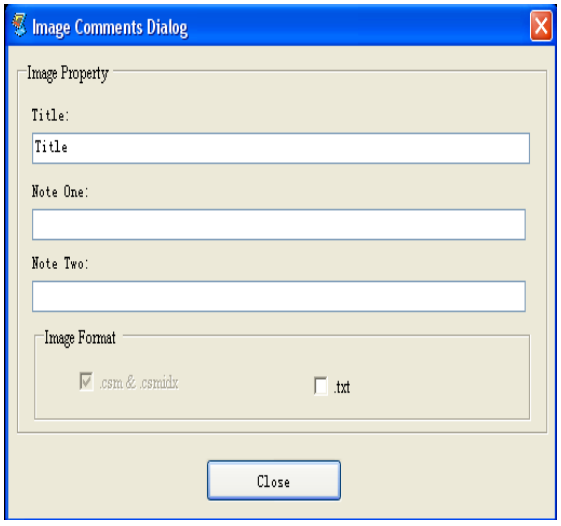
Generally, the probe will have the phenomenon of heat drift when scanning. We can reduce the distortion caused by the heat drift through X/Y non linear correction. (Picture 2-8)

- Image Comments

Name and annotate the graphic. (Picture 2-9)



Picture 2-8 Dialog box of distortion correction



Picture 2-9 Dialog box of setting the information of the graphic

- Potential Coefficient

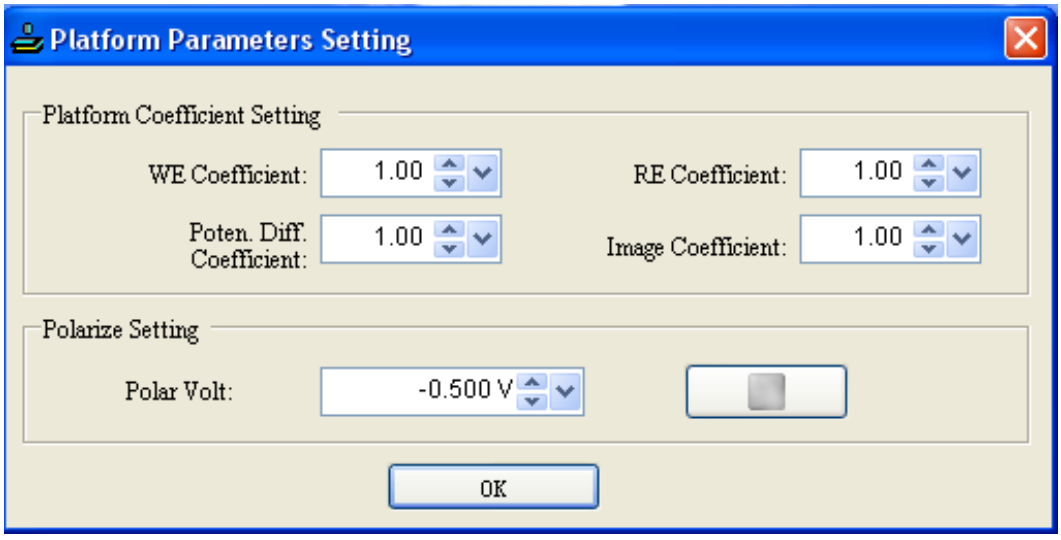
Set the working electrode coefficient, the reference electrode coefficient, the potential difference coefficient and the image coefficient. Besides, we can set the polarization potential of the working electrode and implement scanning under the polarization potential. (Picture 2-10)

- Task Plan

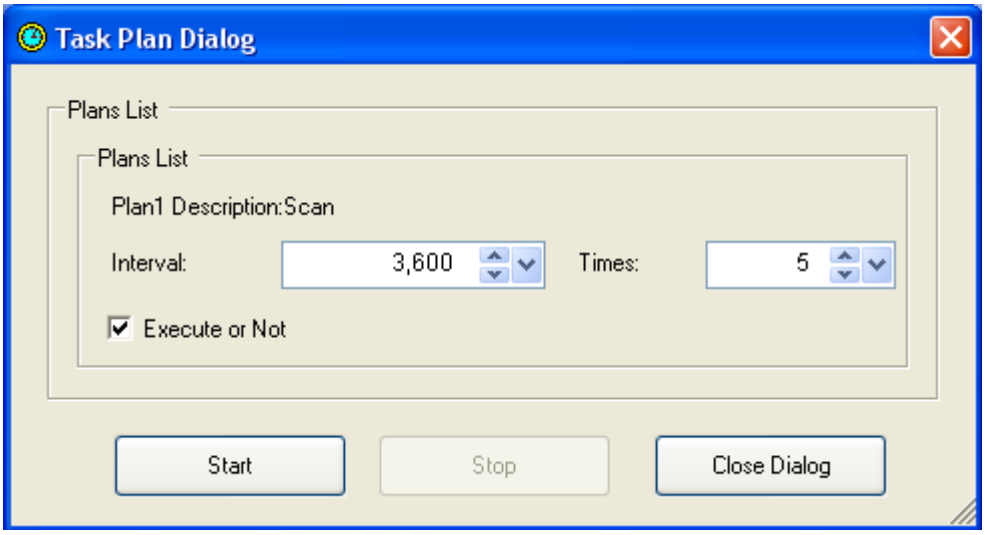
Set the time interval and carry out interval scanning time, i.e., scan at certain interval times. After completing the task, we should return to this sub-dialog to “stop” the task. (Picture 2-11)

- Exit

Close Spm Console (CHS) software.



Picture 2-10 Dialog box of setting the platform



Picture 2-11 Dialog of the task plan

3.1.2 Functions menu

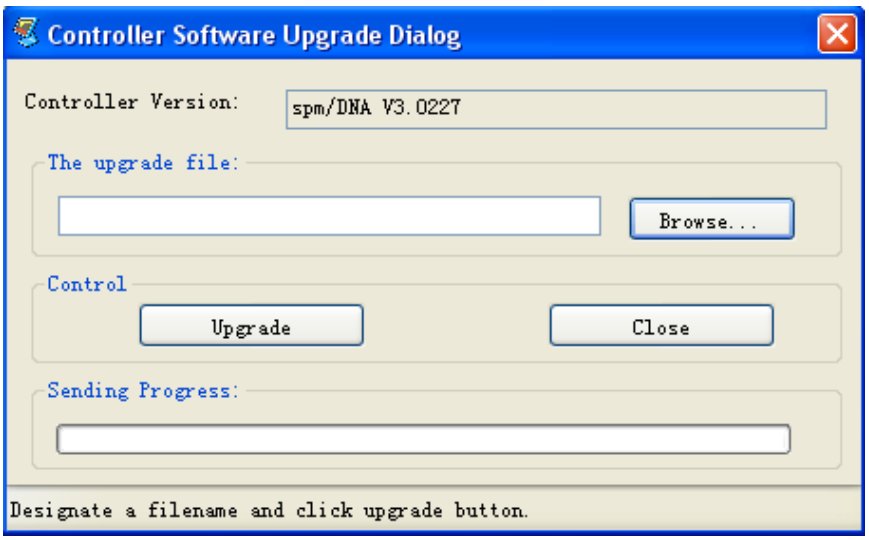
It mainly includes software upgrading and the three-dimensional movement of the control platform.

➢ Functions Upgrade

If the software development has new functions, we can upgrade the functions of the system with the upgrading software provided by the manufacturer to enhance the functions of the system.

➢ Controller Upgrade

It has the access of upgrading software provided by the manufacturer to upgrade the software of the controller. (Picture 2-12)



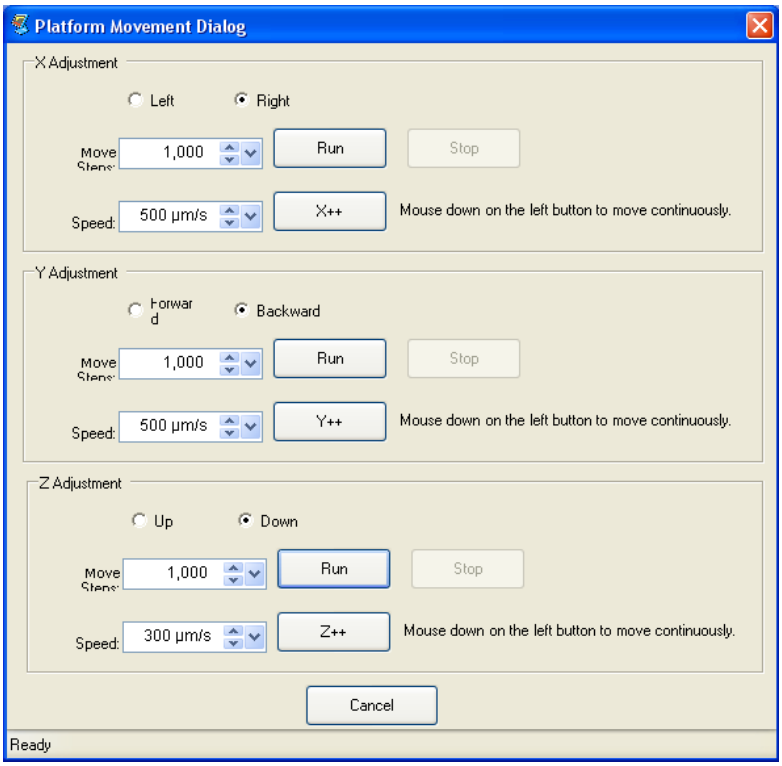
Picture 2-12 Dialog box of upgrading the software of the controller

➢ Platform Movement

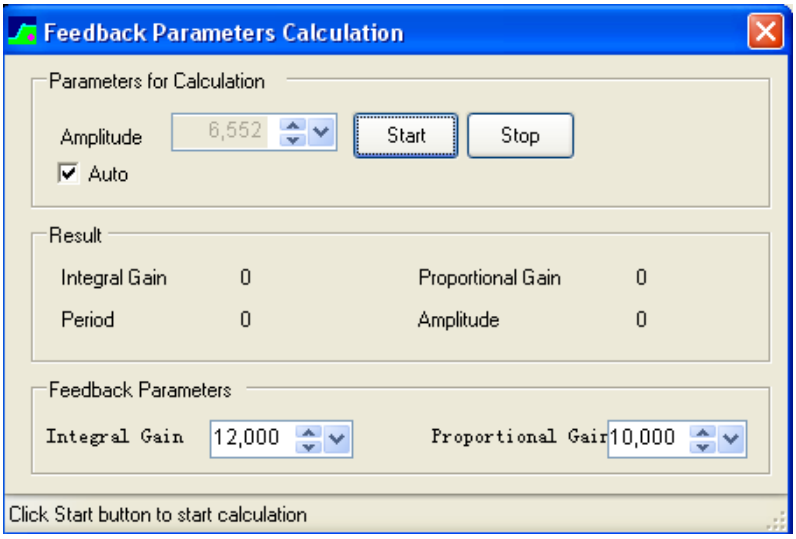
It is used in the three-dimensional movement of exquisite sample control platform. We can move the sample platform through controlling the moved steps of XYZ axis (the step length of Z axis is 50 nm; the axis of X/Y is 100nm). We can also move the sample platform at certain speed. (Picture 2-13)

➢ Feedback Parameters Calculation

We can control the system well with integral gain and proportional gain feedback control. (Picture 2-14)



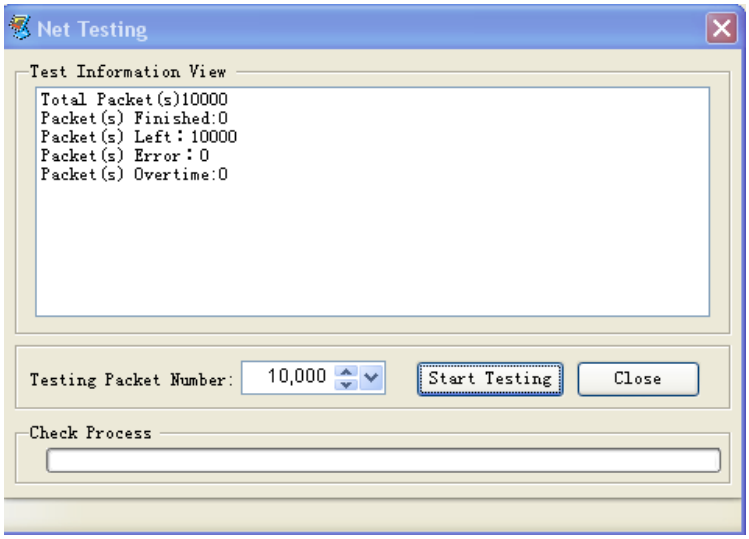
Picture 2-13 Dialog box of the platform movement



Picture 2-14 Dialog box of the feedback parameters calculation

- Net test

Test the working network (Picture 2-15)



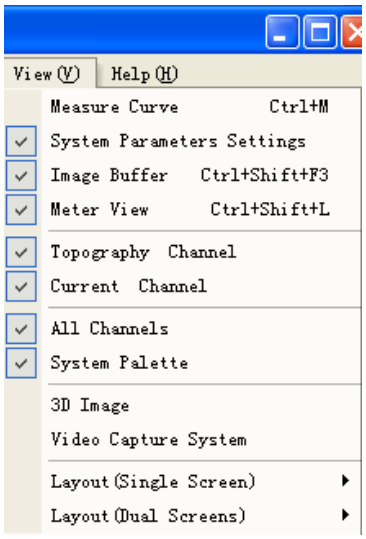
Picture 2-15 Test the network

3.1.3 Language menu

Set the display language of the software, including simple Chinese, complicated Chinese and English.

3.1.4 View menu

It is mainly used to display or hide the sub-window of the operation interface. The chosen window will be shown in the signal switch window at the bottom of the interface. (Picture 2-16)



Picture 2-16 View menu

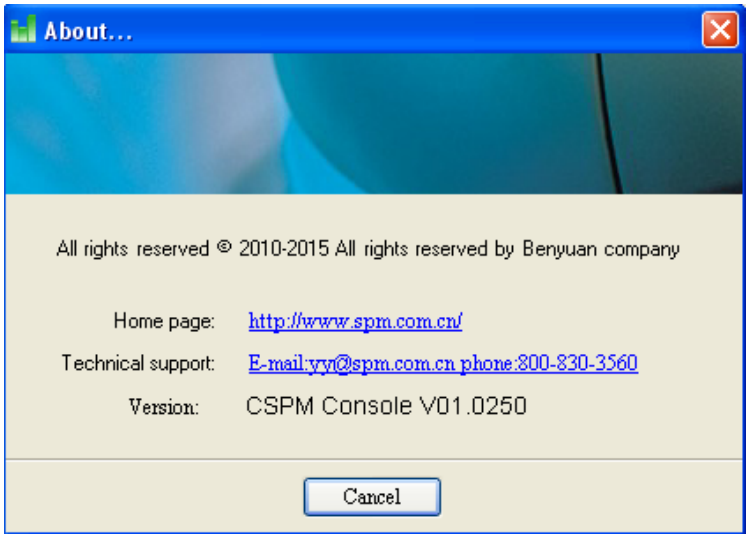
3.1.5 Help menu

➢ What's new?

Open the detailed explanation of the version.

➢ About

Open the "About" window; and it shows the instrument version, the information of the company, etc. (Picture 2-17)



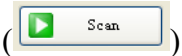
Picture 2-17 Dialog box of "About CSPM On-line Control" Software

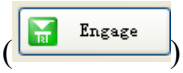
3.2 System parameters settings

➢ System Status

Generally, when we start the software, it will connect the host automatically in the initialization process.

➢ Control

The shortcut button of scan (

) is used for scanning after the completion of engaging probe; the shortcut button of engage (

) is used for engage automatically, withdraw, run single and levelling adjustment. When you click the shortcut key of engage, the dialog box shown in Picture 2-18 will appear.

Picture 2-18 Dialog box of engage

- Continuous---After scanning the previous image, it scans the next image immediately.
- Dual---It collects date both when the needle moves toward the left and the right (forward and backward) and gets two images.
- Cycle---After it scans the previous image, it scans the image back to forth immediately.

➢ Image Settings

- Resolution---Set the resolution of the image, i.e., the number of collected dots.
- Aspect ratio (height: width)--- Set the shape of the image.

➢ Working Mode

It includes four working modes, i.e., scanning reference electrode test (SRET), scanning tunneling microscope (STM), scanning current test (MI) and scanning reference electrode - scanning tunneling microscope joint test (SRET-STM). When the working mode changes, the scanning parameters will be changed accordingly.

➢ Scanning Parameters Setting

- Scan direction---Set the scanning direction of SRET (left / right / upward / downward);
- Scan size---Set the range of the scanning area
- Scan rate---It decides the scanning speed, i.e., the lines it scans every second. For example, if we set it as 0.8, then it scans 0.8 lines every second.
- X/Y direction---It can be used to adjust the scanning position.
- Feedback type---It is used to set the feedback pattern in the scanning STM mode (logarithm/linear). Generally, we choose the logarithm pattern.
- Scan angle---It is used to set the scanning direction of the STM mode. We can obtain an ideal image through adjusting the scanning angle.
- Bias ---We can set the initial current signal value through adjusting the bias voltage. The value of the signal should not be too large in case of the failure in needle approaching.
- Set point---In order to obtain a good scanning image, the system must control the interaction between the probe and the sample accurately. Through the electrical control circuit, the system controls the extension in Z direction of the piezoelectric ceramic, which enables the interactive force between the probe and the sample equals the reference point set by the user (Under different working modes, the interactive force between the probe and the sample is different, so is the significance of the reference point), thus protecting the probe from colliding with the sample. Besides, through recording the voltage of the piezoelectric ceramic in Z direction, we can get the morphology of the surface of the sample.

The user sets the reference point to maintain the operation of the feedback circuit. The reference point emphasizes that the feedback circuit must maintain the steady interactive force between the probe and the sample.

- Proportional gain---The feedback circuit calculates the error of the actual interactive force between the probe and the sample and the set reference point at certain intervals. The proportional gain controls the speed of the compensation for the error. The larger the proportion gain is, the more acute the feedback is. Proportional gain only cannot make the feedback circuit steadily work on the reference point set by the user. The system will have certain errors. In other words, the system can only approach but cannot reach the set reference point.
- Integral gain---It is used to make up for the accumulated systematic error. In the system, if we only use the proportional gain, the system will have errors more or less. Therefore, the system has to know whether the total error of the interactive force between the probe and the sample and the error between the reference points increase or reduce at certain intervals. The integral gain is to make up for the accumulated systematic error during this period. The larger the integral gain is, the more acute the feedback is.
- Reference gain---For a majority of samples, the morphological data obtained through scanning is consecutive to those in the last line. Therefore, the system introduces the parameter of reference gain. Through recording the data obtained in the last line, we can predict the morphological data of the current scanned line.

Because of the consecutiveness of the morphological changes of the samples, reference gain is more effective for the samples whose morphology is regular or cyclical, such as raster.

- Data display

- Signal---It displays the value of the channel current. In the scanning channel mode, the value of the channel current changes with the distance between the needle tip and the surface of the working electrode. The piezoelectric ceramic maintains the current unchanged through adjusting the distance. We can get the morphology of the surface through recording the adjustment value of the voltage.
- Z voltage---The voltage added to the piezoelectric ceramic with the change ranging from -180～＋180V. In the scanning tunneling microscope mode, Z voltage changes with the adjustment of the distance between the needle tip and the surface of the working electrode. In the mode of the SRET, the voltage added to the piezoelectric ceramic is fixed, so the displayed value remains unchanged.
- WE---The voltage of the scanning probe
- RE---The voltage of the reference probe
- Potential difference---The potential difference value between the scanning probe and the reference probe.

3.3 Real-time Display Window of Two-dimensional Signal

- It displays the collected date in the form of images. The shade of the color in the image indicates the scale of the potential.

3.4 Image Buffer Area

It is used to store the scanned image temporarily. It is suggested that the image should be stored under the catalogue of target after scanning.

3.5 Parameter Setting

- Size Grid

  It is used to display the changes of the data in single line in real time.

- Waveform parameter

- Trace---When we select it, the waveform will be on display; when we cancel the selection, the oscilloscope will not show the waveform.
- Save--- The dialog box will pop out and the waveform on display store can be stored, when it is clicked.
- Auto refresh---When we select it, it will display the changes of the waveforms of each line with scanning dynamically; when we cancel the selection, the waveform will stop at the time of cancellation.
- Background rejection---In SRET mode, the surface potential is generally large, it will glass over some small potential peaks/valleys which can indicate the surface changes. So it can reject the basement potential to display the potential change more clearly. When the selection is cancelled, you need to add signal bias voltage to display the graphic generally. Therefore, the background rejection need to be choose generally in SRET.
- Surface fit---In STM mode, the leaping data may occur because of the impact of the external factors. Generally speaking, when the correction of curved surface is 0-3 order, the impact causing leaping data can be weakened.

- Parameter setting

- Lowpass filter---It is used to get rid of the impact of the noise.
- Gain---It adjusts the magnification times according to the image after scanning so as to optimize the data within the display range. Generally, the magnification times in SRET mode is 100 times.
- Brightness---Set signal biasing according to the surface potential so as to make the signal value within the displayed range.
- Z-limit ---Generally, in the STM mode, it cancels automatic extension adjustment and adjusts the extension range to maximum (360V).
- Save the image or not---In selection, it will automatically store the scanned image into the image buffer area. When it is not selected, we should save the image manually after scanning.

3.6 Signal switch window

It is used to display multiple windows. The window on display can be selected in the view menu.

3.7 Status bar

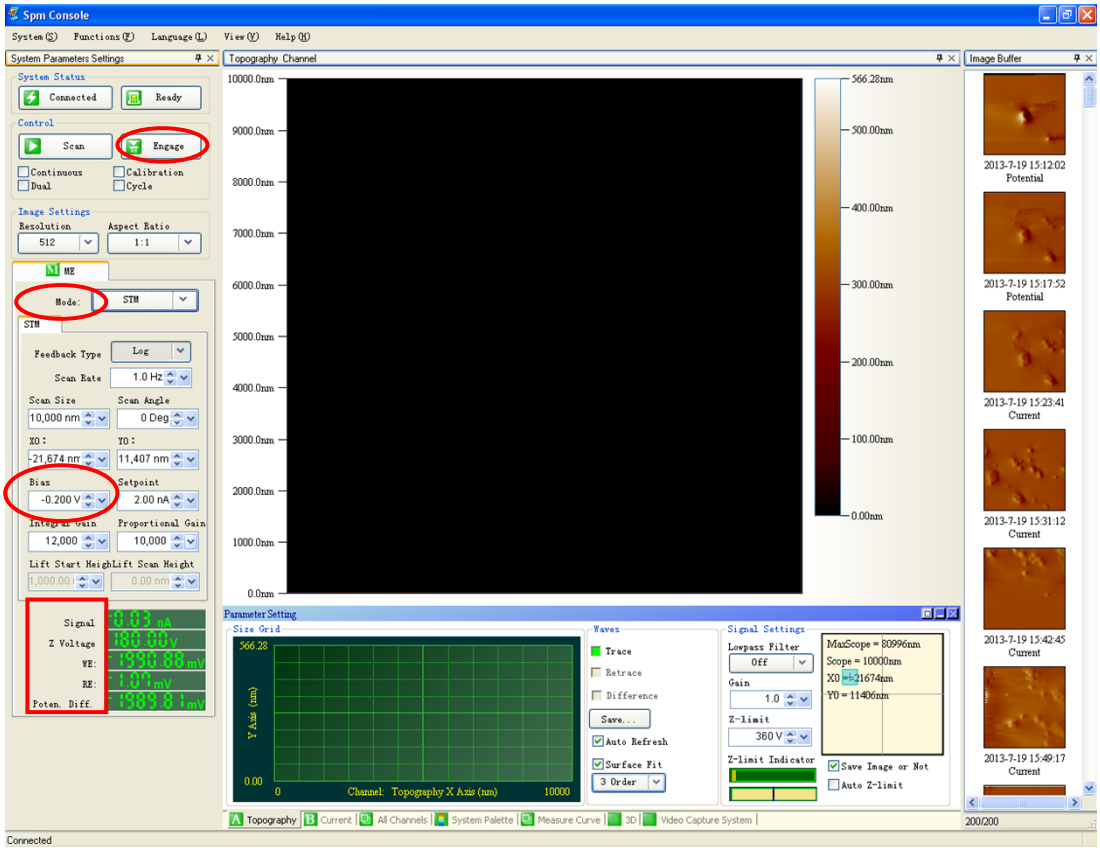
It is used to display the working status of the system.

Chapter 3 Introduction of working modes

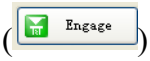
1 Scanning tunneling microscope (STM)

1) Fix the working electrode upon the scanner and level the sample with the horizontal spirit bubble. After the installation (adjust the probe to the scanning area where you are interested), turn on the controller and host successively and then enter the working interface of the software. After opening the working interface, the software will connect the main controller automatically. If the connection is normal, the bottom of the working interface will display “Controller initiating”; if the connection is abnormal, restart the main controller (Picture 3-1).

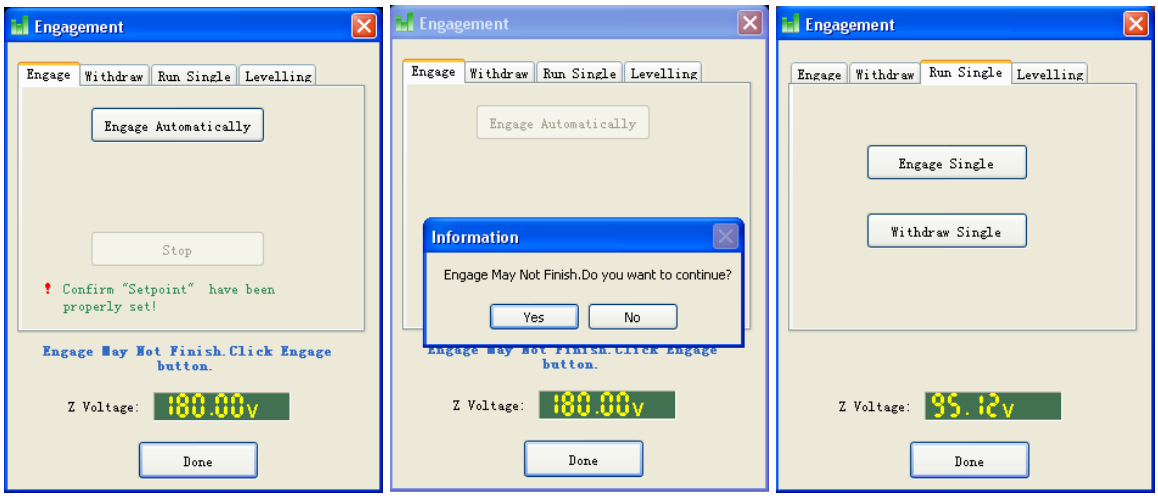
2) The system parameters setting window selects the “STM” as the working mode and chooses appropriate resolution. The value of “Signal” in the signal display window at the bottom shows that the value is around 0nA and that Z voltage is 180.00V, as shown in Picture 3-1. If the displayed absolute value of “Signal” is large, (e.g. larger than 1nA), there may be interference around. You should check whether the metal box cover where the probe is fixed is closed or not. If it is closed, we can adjust the value of “bias” in the scanning parameter window to reduce the signal.



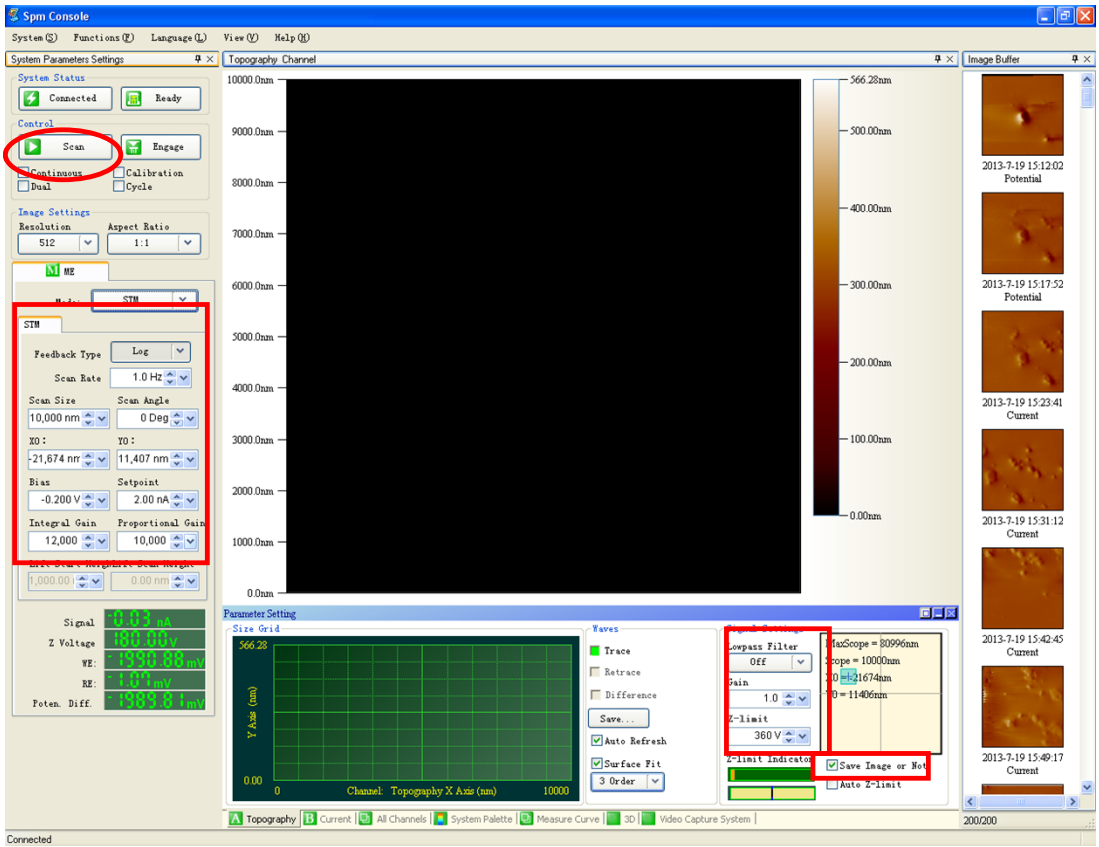
Picture 3-1 Selection of working patterns

3) First, use the main controller to shorten the distance between the probe tip and the surface of the electrode. Choose the engage button (

) in the “System parameters setting), then the “Engage” will appear (on the right in Picture 3-2). Click the “Engage automatically” in “Engage” window, and the scanning probe will move approach to the sample automatically. If the approaching is not completed, the reminding window will pop out (on the middle in Picture 3-2). After the probe approaching, the Vz voltage shown in the window will fluctuate around less than 180.00V. Switch the window to “Run single”. (on the left in Picture 3-2). Click “Run single” until the displayed voltage is around 50V; and then click “Done”.

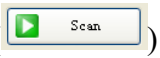


Picture 3-2 Engage window



Picture 3-3 Scanning parameter setting

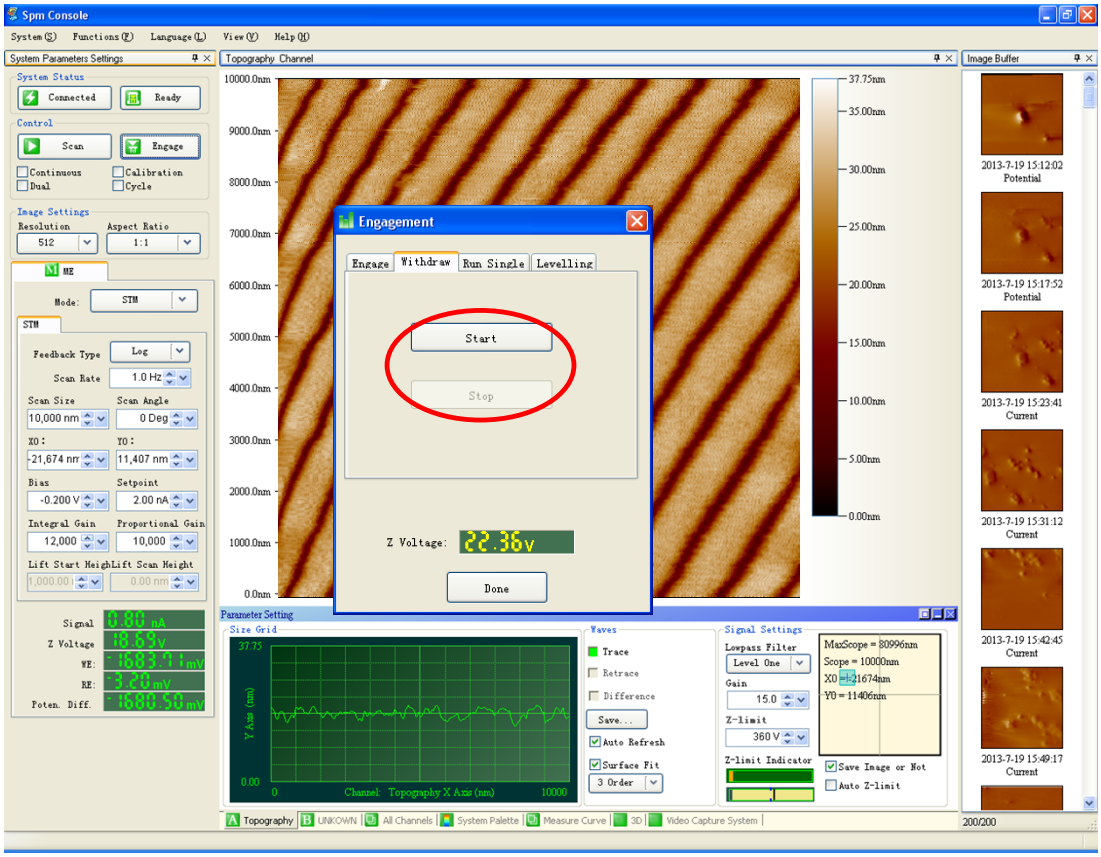
4) After the completion of probe approaching, we should set the parameters in need in the scanning parameters setting (Picture 3-3), such as the scanning range, scanning frequency (refer to the lines scanned every second. For example, if we set the frequency as 0.8, then it scans 0.8 lines every second) and so on.

5) Click “Scan” (

) in System parameter setting window to begin scanning. In the scanning process, we can adjust the “Lowpass filter” and “Gain” (Picture 3-3) in Signal parameter setting window properly according to the scale of the signal so as to get clear morphological image whose details can also be seen.

6) After the scanning, click the button of “Engage” (

); choose the withdraw interface (Picture 3-4) and click withdraw (2mm or 5mm);



Picture 3-4 Withdraw interface

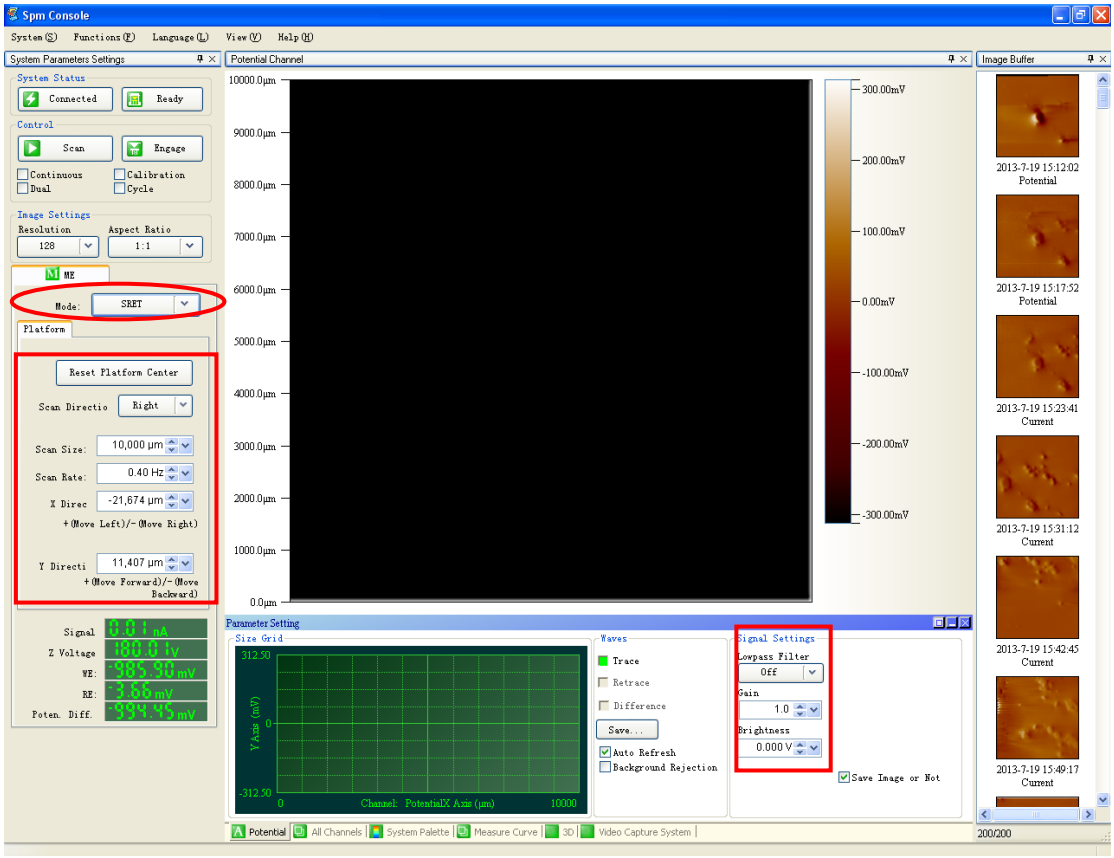
7) Take off the probe and working electrode; and turn off the working software, controller and host successively.

2 Scanning reference electrode test (SRET)

SRET requires fixing the distance between the probe and the sample accurately. In order to realize the goal of automatic and accurate control, STM assistant automatic

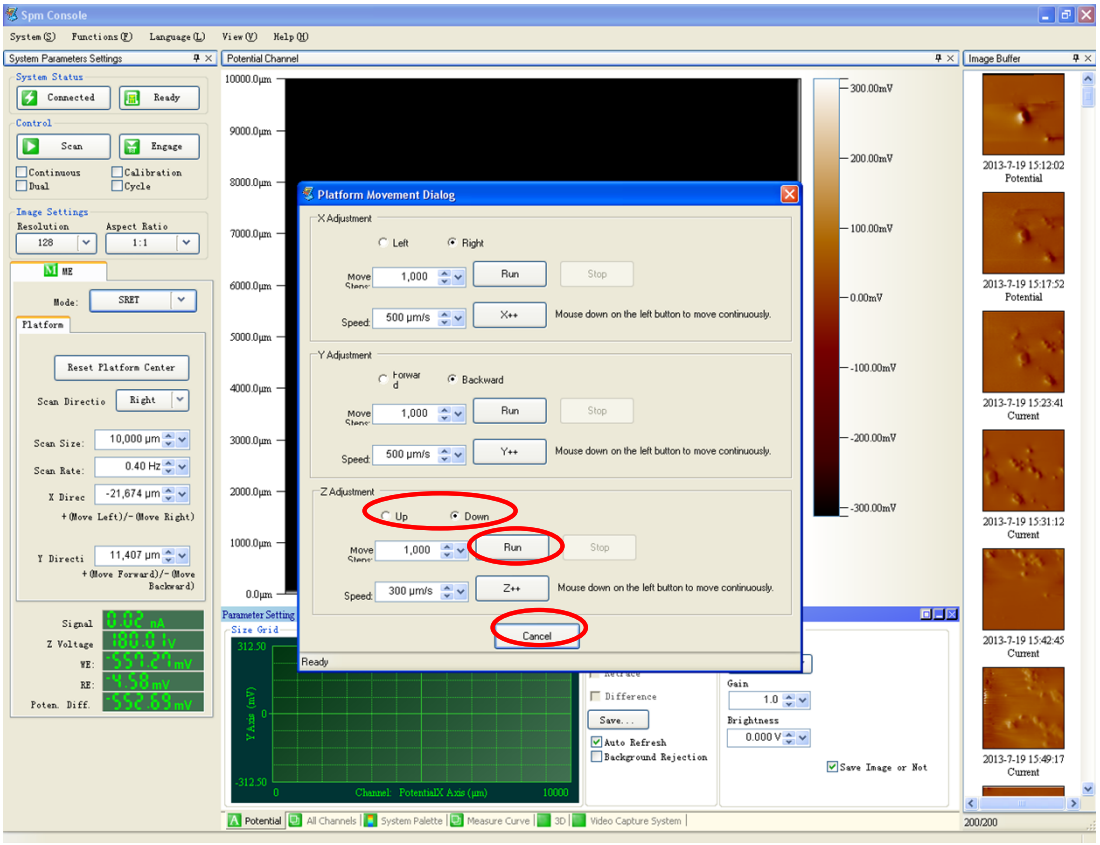
probe approaching pattern is adopted in XMU-BY-LG Scanning Electrochemical Workstation. As a result, the first two steps are consistent with those in the scanning tunneling microscope, i.e., approach the probe automatically to the surface of the sample through controlling the tunneling current.

1) Refer to Step (1) and (1) in STM Measurement.



Picture 3-5 SRET interface

2) “Engage” is completed when the voltage is less than 180 V. Don’t need for “Run single”. After returning to the working interface, we should adjust the working mode to “SRET” and choose “Function” menu---“Platform movement” (Picture 3-5). Move the platform upward for 500-1000 steps (50nm for every step). After completing it, we can close the dialog box (Picture 3-6).

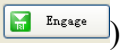


Picture 3-6 Movement of three-dimensional platform

3) Set the scanning parameters in the System setting window, such as the scanning direction, range, frequency etc..

4) If the sample is partly eroded obviously, the partial difference is quite large and that the signals of the scanning electrode and reference electrode are steady in the testing environment, you may not require choose the “Background rejection”. Otherwise, you’d better choose “Background rejection” and set magnified times in the Signal parameter setting window to 100 times.

5) Add the research solution in the sample surface and then begin scanning.

6) After the completion of the scanning, click the button of “Engage” (

) and then choose the withdraw; click withdraw (2mm or 5mm)

7) Take off the probes and working electrode. Close the working software, controller and host successively.

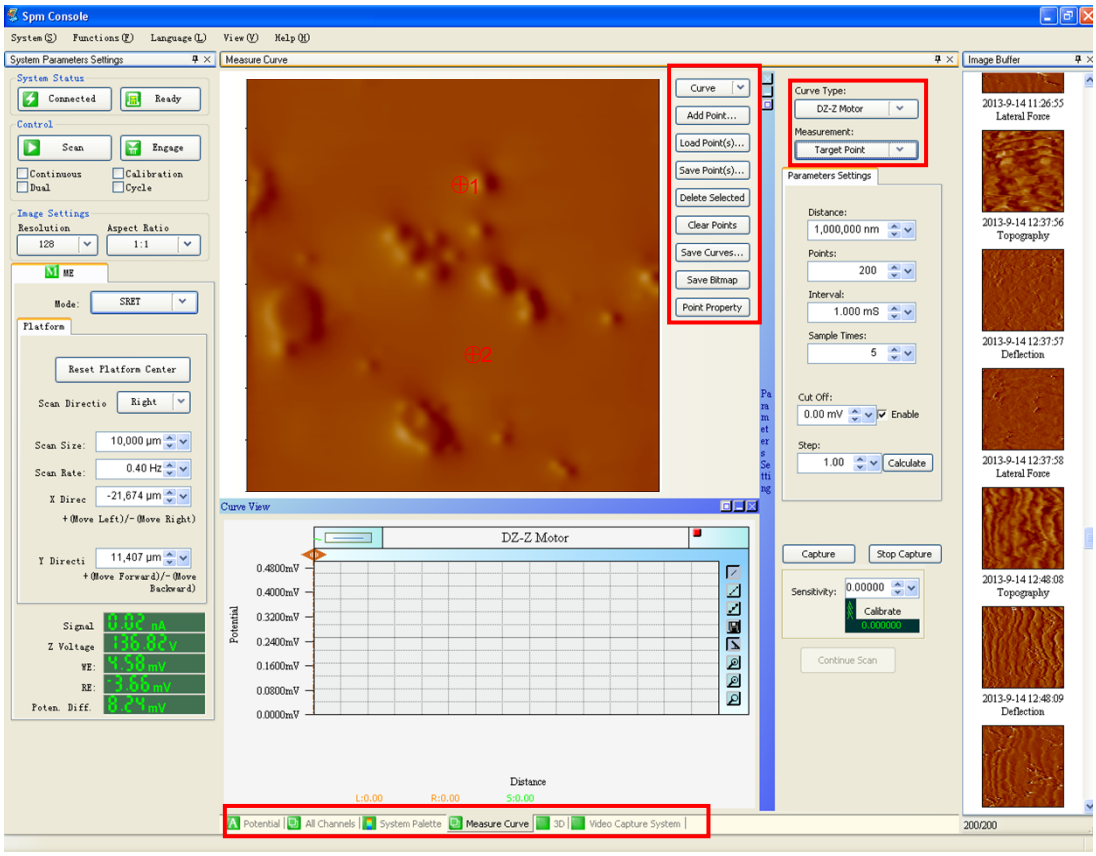
3 SRET-STM Measurements

SRET-STM Measurements are mainly applied in the association research of the partial electrochemical behavior of the electrode surface and the micro morphology of the electrode surface. The key point of the test is to obtain the electrochemical distribution information through the SRET; then choose the position it is interested in to carry out the *in situ* STM morphological change research/ In the testing process, the two working modes use the same probe, which requires that the probe should both satisfy the needs of SRET and the needs of STM test in the solution environment. At current, the Pt-Ir needle prepared by our research group has basically met the requirements of the test. The approach is mainly divided into three periods: (1) SRET *in situ* potential distribution test; (2) Position the needle into the area that it is interested in; (3) STM morphological test.

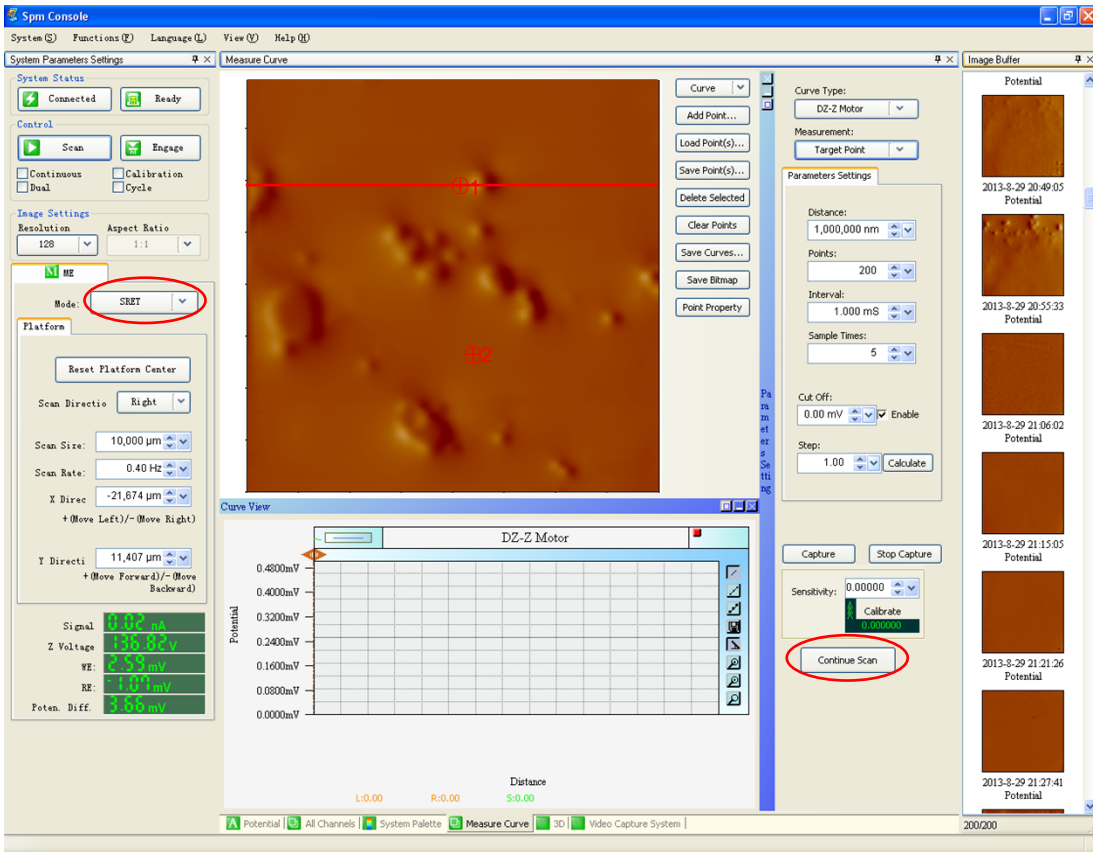
1) Refer to Approach 2 for the SRET test;

2) Position the probe into the area that it is interested in: (a) After getting the eroded potential graphic by using SRET, open “Measure curve” and “Curve type” to choose “DZ-Z motor”; and open “measurement” to choose “Target point”; (b) Choose the points which need scanning the morphology in the graphics (double click the position of the point). Remove the chosen points through the button on the right side of the graphic display area. We can also get the information of the positioning points from the “point property” (Picture 3-7); (c) After selecting the positioning points, we

can click “Scan” in the system parameter setting window. When it scans the chosen position, it will stop scanning automatically. (Picture 3-8)

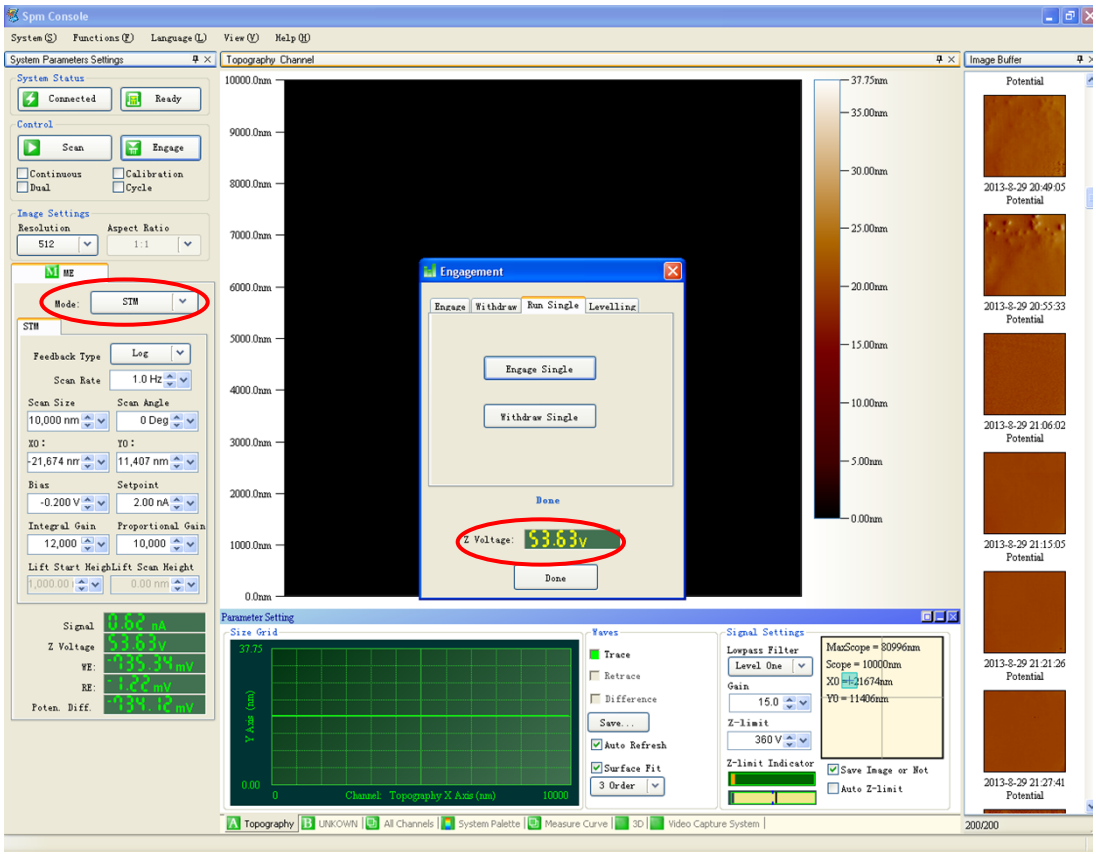


Picture 3-7 Position point scanning



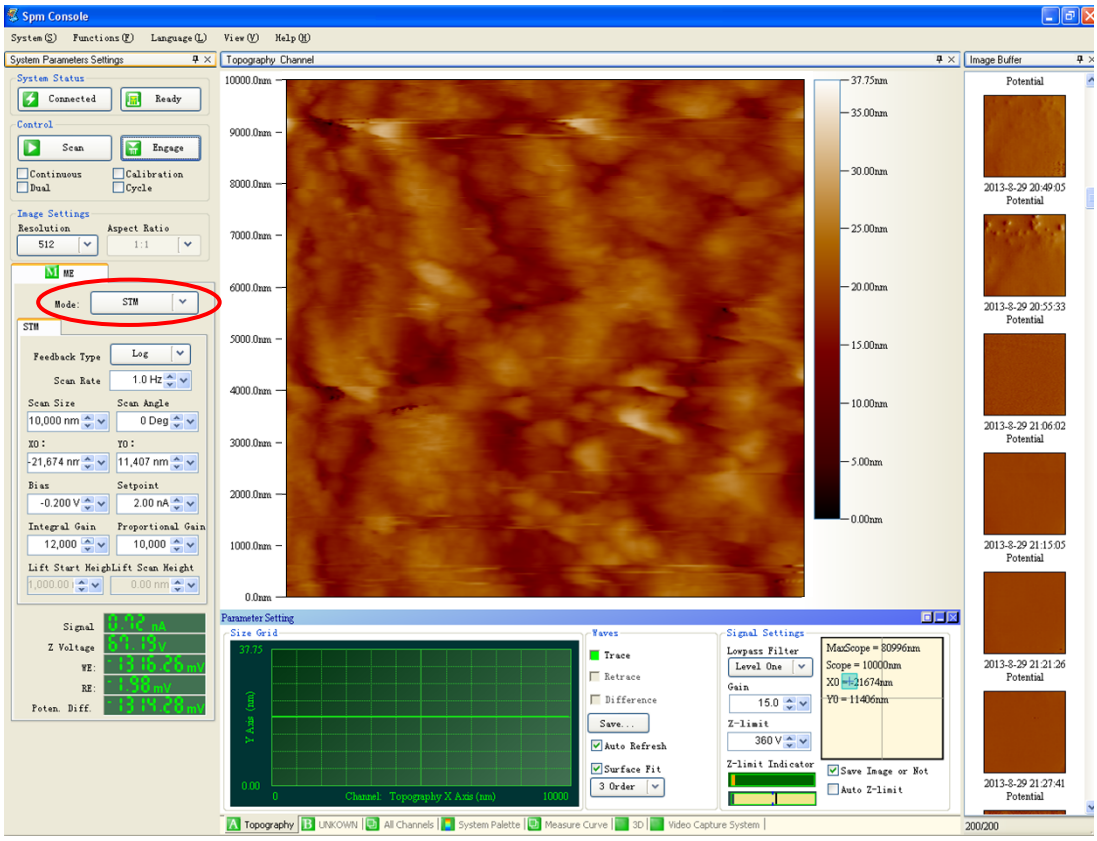
Picture 3-8 SRET and STM switch

3) Scanning tunneling microscope test: After completing the above steps, shift the scanning mode into the STM mode. Engage the scanning probe until the Z voltage value reaches around 50V (Notice: if the probe tip is not well sealed, the potential display value will turn into -180.00V after changing the working mode. STM scanning is not allows at this time); set the scanning parameters (such as the scanning range and so on) (Picture 3-9). Refer to Chapter 2 for the detailed parameter explanation.

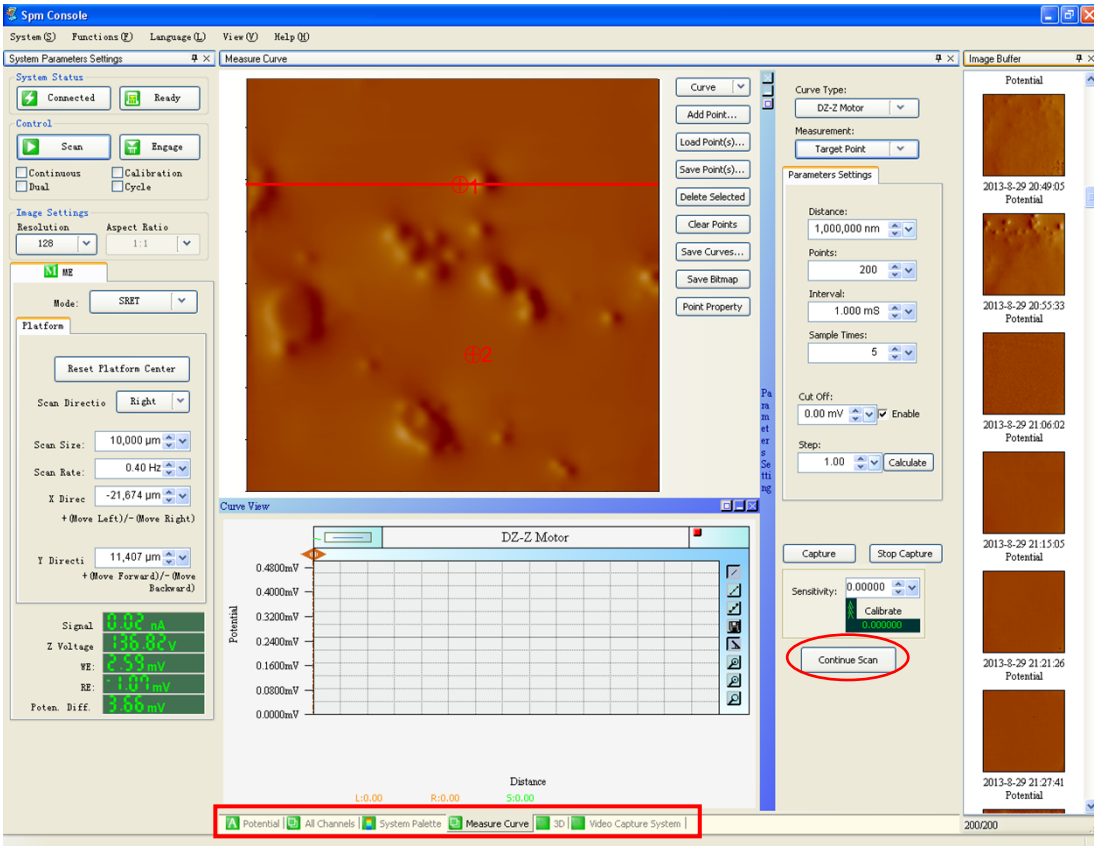


Picture 3-9 Engage the probe after the working mode shifts to STM

4) When morphological scanning test completes and if we still want to test the potential distribution on the surface of the electrode, we can change the working mode into “SRET” (Picture 3-10); then we can choose the menu of “Function”---“Platform movement”. Move the platform upward by 500-1000 steps, after completing which we can close the dialogue. Then we choose “Measure curve” and click “Continue scan” at the right button of the interface (Picture 3-11). The potential distribution test will continue scanning from the positioning point.



Picture 3-10 Switch the working mode



Picture 3-11 Continue scan the SRET potential distribution

5) When the selected area which it is interested in is more than one, the system will also stop scanning after scanning to the next positioning point and wait until the user finishes the morphological scanning as above. Then the system repeats this until the test of the entire target points finishes (Pay attentions to the change of engage/withdraw probe and the scanning parameters when shifting the working modes).

6) After the scanning, click the button of "Engage" (

), choose the withdraw interface and then click start (2mm or 5mm).

7) Take off the probes and working electrode; and then close the working software, controller and host successively.

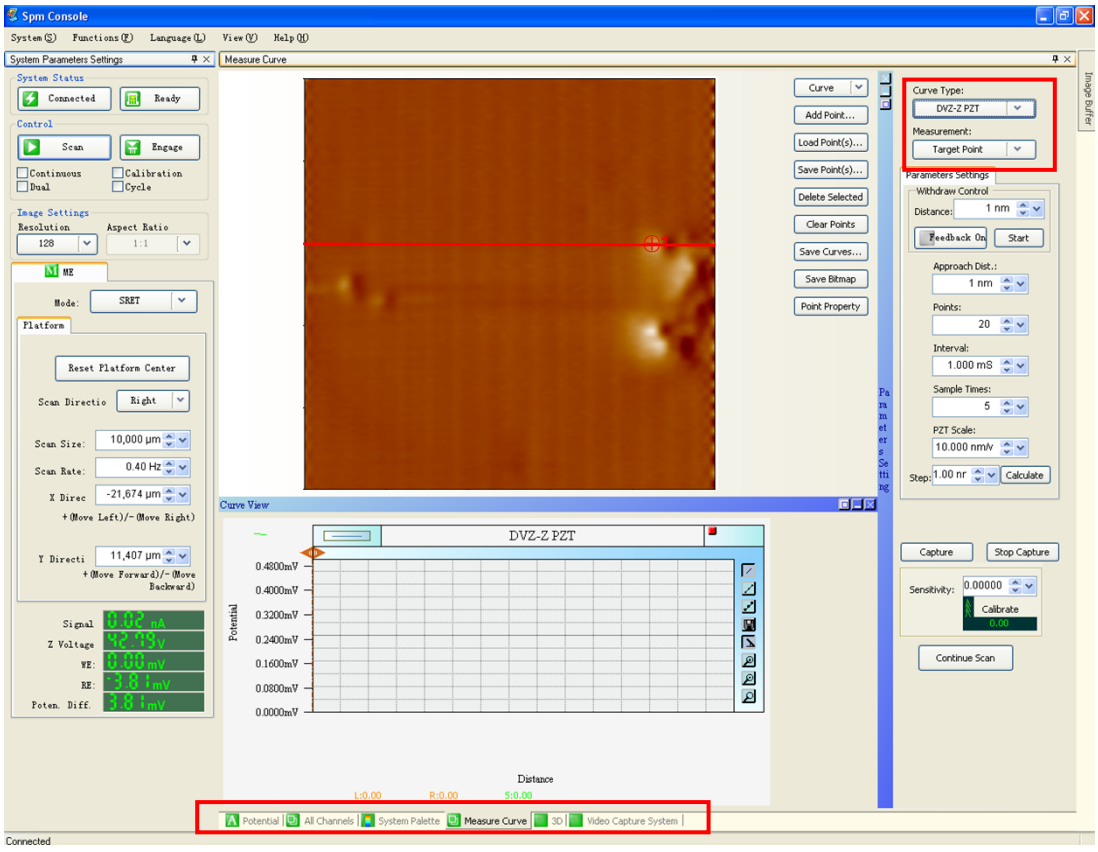
4 The Potential Measurement around the Target Point

The test of the information of the potential around the target point can used to carry out the potential section line test on the three-dimensional direction (X/Y/Z) on the partial points, thus obtaining the multi-directional electrochemical information on the partial points. In addition, when we pay attention to single corrosion active point, we can greatly improve the experiment efficiency and time resolution through monitoring the change of one-dimensional potential distribution. The test process is mainly divided into three periods: (1) SRET *in situ* potential distribution test; (2) Position the scanning probe to the area it is interested in; (3) one-dimensional potential distribution test.

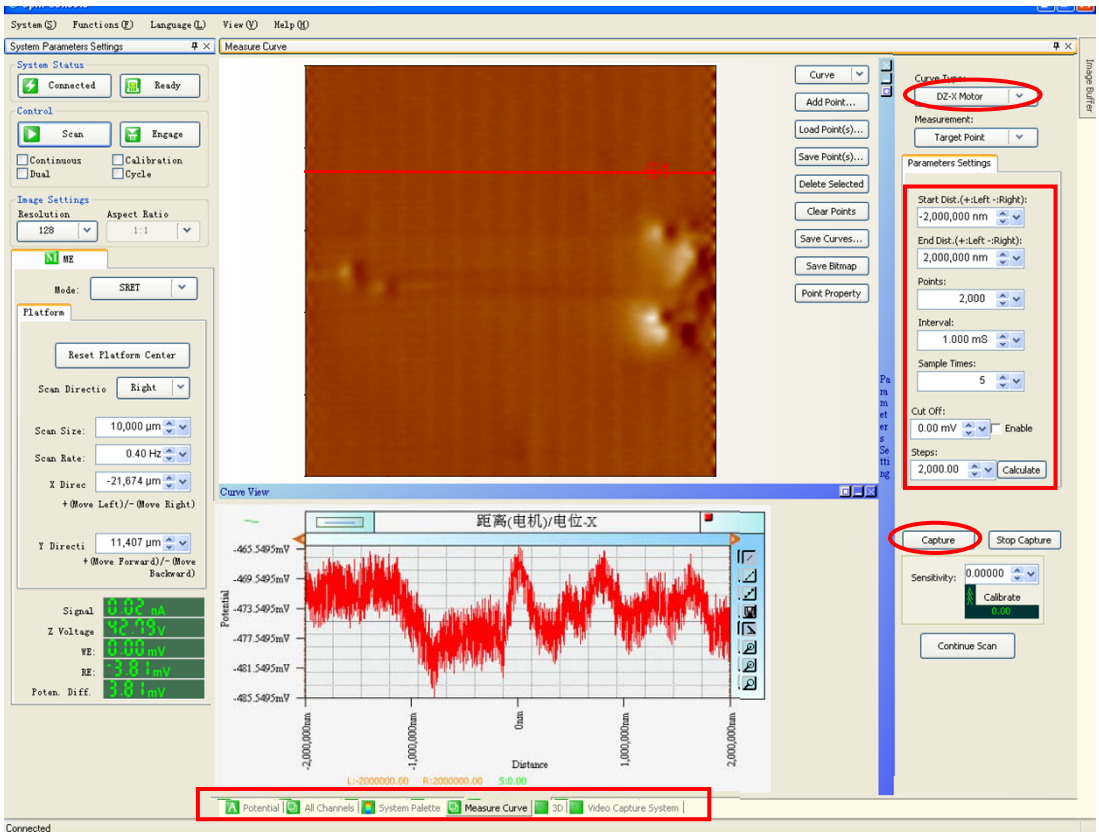
The detailed steps are as follows:

1) After getting the corrosion active potential graphic by using SRET potential scanning, open “Measure curve” and “Measurement” to choose “Target points” and open “Curve type” to choose “DVZ-Z PZT”; and choose the points to be studied in the obtained graphic (double click the position of the point). (Picture 3-12)

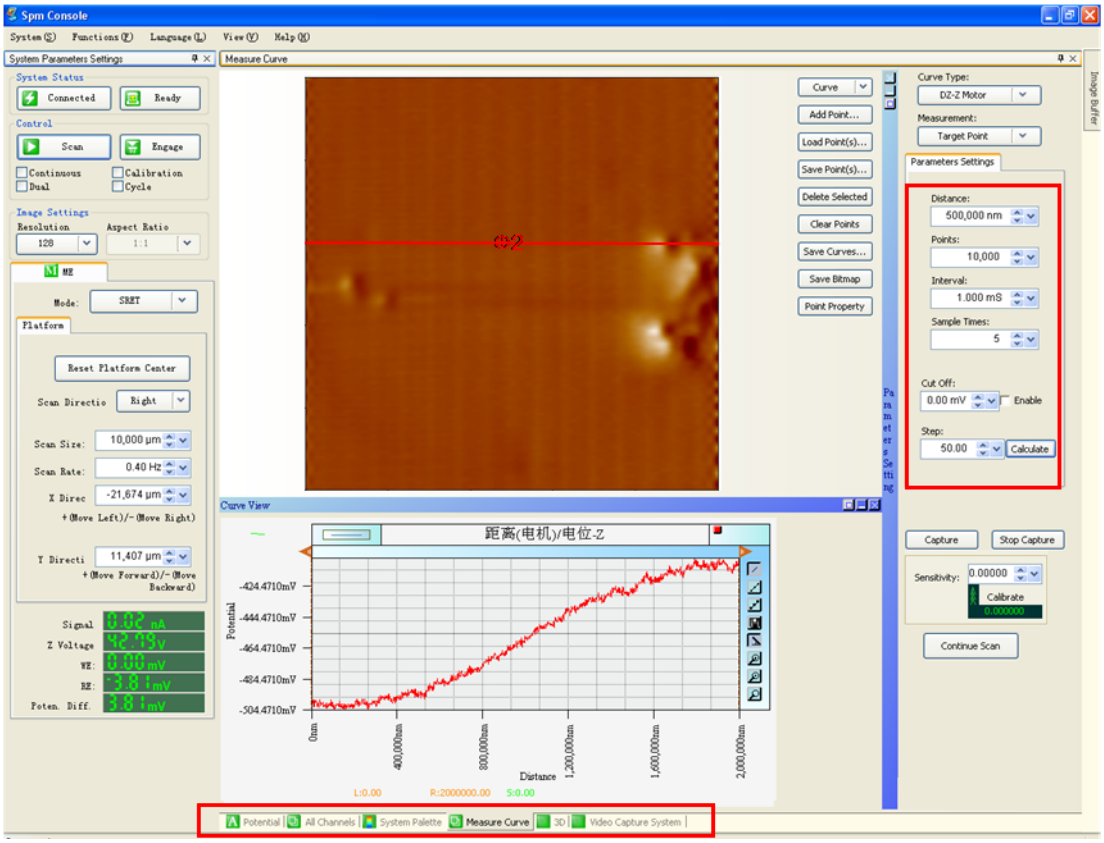
2) After selecting the positioning points, we can begin scanning. When it scans the target point, it will stop scanning. If we want to get the potential information of the X(Y) axis of the positioning points, we can select the “Curve type” as “XZ-X motor” (Picture 3-13); If we select the “Curve type” as “DZ-Z motor”, we need to engage the scanning probe appropriately (Picture 3-14).



Picture 3-12 Determination of target points



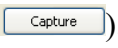
Picture 3-13 Potential test of X axis



Picture 3-14 Potential test of Z axis

3) In “XZ-X motor” or “YZ-Y motor” window, we can set the scanning parameters, such as the distance at the beginning and at the end, the number of the collected points and so on. After the parameters are set, click the button of calculation (

); adjust the scanning parameters and control the step length more than 50nm.

4) After the parameters are set, we can begin measurement (

). Then after the measurement, the results will show in the “Curve view”. We can save the results with the save button on the right side of the window.

5) After we measure the information around the points, we can adjust the curve type into “DVZ-Z PZT” and click “Continue Scan” (

)

6) After the scanning, we can withdraw the probe (2 mm or 5mm); take off the scanning probe and working electrode. Then we can close the working software, controller and the host successively.

5. Micro-current Measurements (MI)

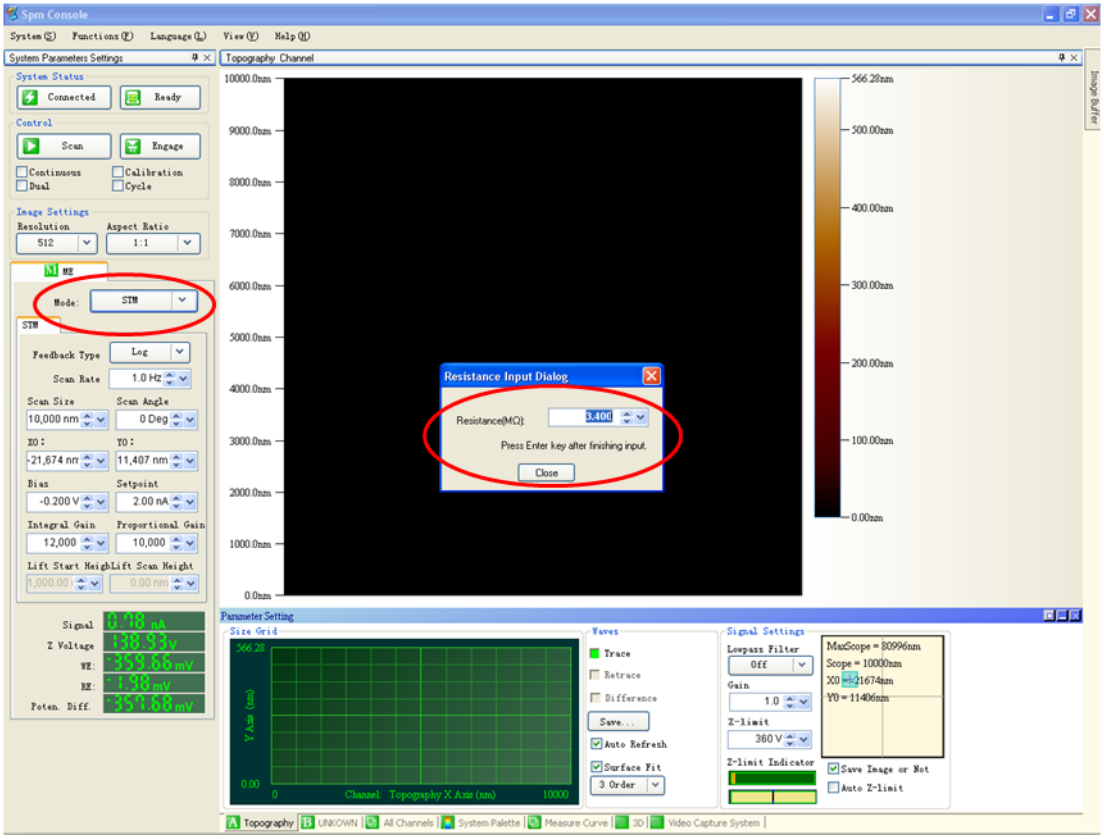
MI requires fixing the distance between the probe and the sample accurately. In order to achieve this goal automatically and accurately, STM assistant automatic probe approaching pattern is adopted in XMU-BY-LG Scanning Electrochemical Workstation. So the first two steps are consistent with those in STM mode, i.e., approach the probe automatically to the surface of the sample through controlling the tunneling current.

The measurement principle of voltaic probe: When the two insulating microelectrodes close to horizontal distance each other but with certain height difference, the measured potential of the two probes can be thought to be located in

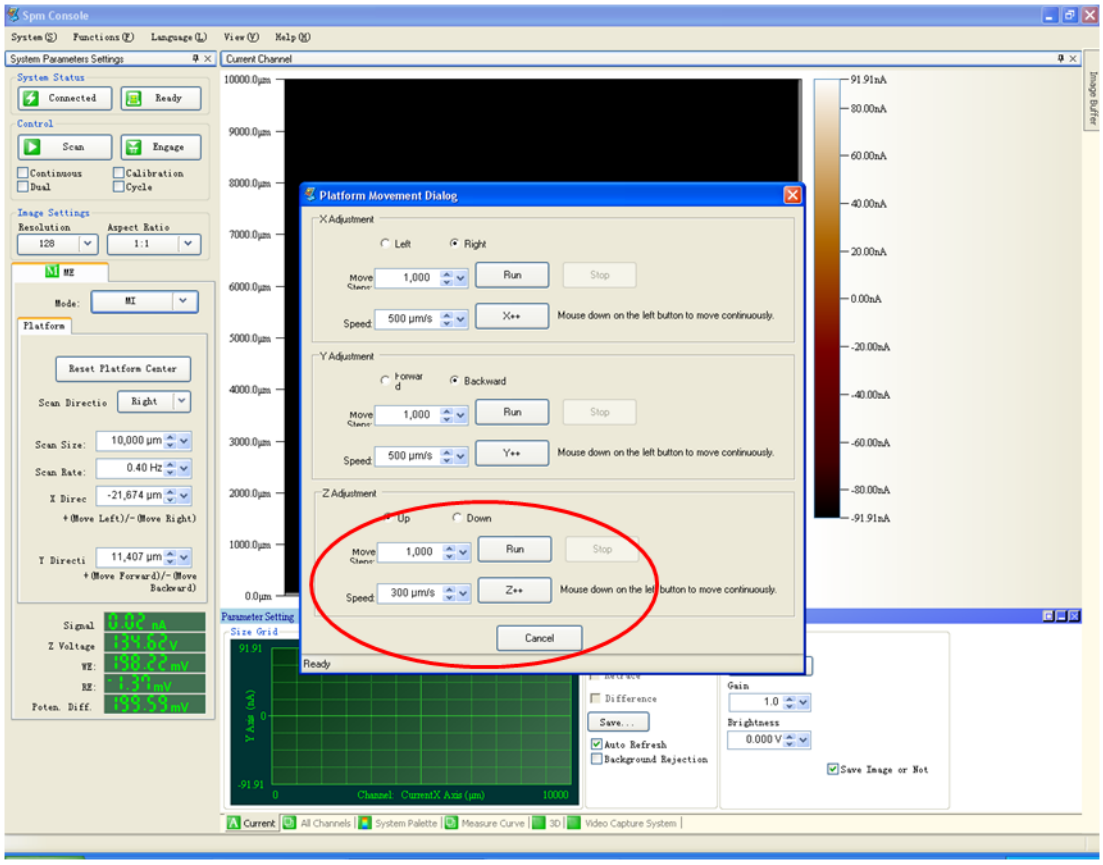
the same vertical direction (refer to the sample surface). Therefore, the local voltage drop in this direction can be obtained based on the potential difference between the two probes, eventually, the local current in the direction can be monitored. In general, the current of vertical direction is maximum in the centre of corrosion site, that's to say, the voltage drop in same site is maximum, and this site also is the peak of current density over the sample. Therefore, the current measurements can gain a better sensitivity than the SRET.

1) Refer to Step (1) and (1) in STM Measurement (Notice: the voltaic probe contains two micro probes. The probe with a long wire should be connected to the scanning probe, while another with a relative short wire should be connected to the reference probe).

2) In STM mode, Engage automatically until the voltage is less than 180V. Don't need for "Run single". After returning to the working interface, adjust the working mode to "MI" and enter the solution resistance (estimate generally), remember press the "entre" key, then close the dialog box (Picture 3-15).



Picture 3-15 the interface of local current measurement



Picture 3-16 Movement of three-dimensional platform

3) Choose “Function” menu---“Platform movement”. Move the platform upward for 500-1000 steps (50nm for every step) (picture 3-16). Close the dialog box after finish.

4) Set the scanning parameters in the System setting window, such as the scanning direction, range, frequency etc..

5) You are suggested to choose “Background rejection” and set magnified times in the Signal parameter setting window to 100 times.

6) Add the research solution in the sample surface and then begin scanning.

7) After the completion of experiment, withdraw the probe.

8) Take off the probes and working electrode. Turn off the working software, controller and host successively.

6. Micro-[Cl^-] Measurements (Cl^- Distribution)

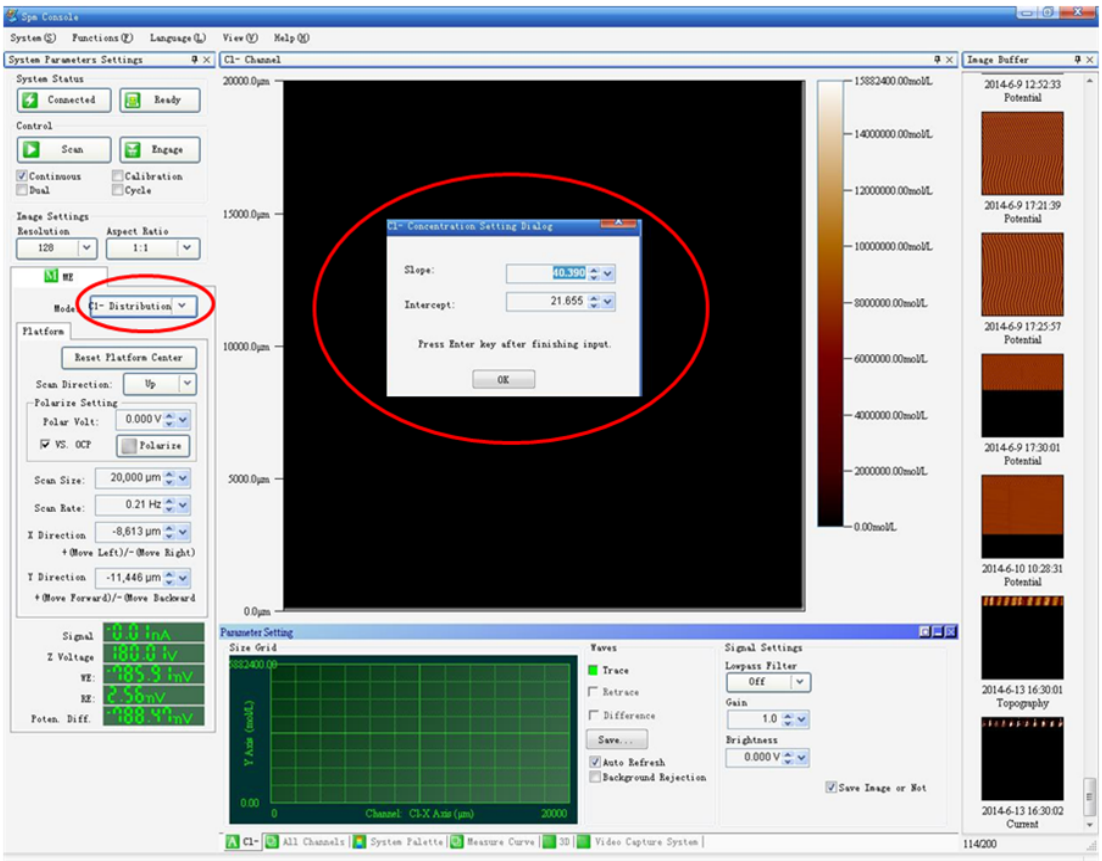
Cl^- distribution also requires fixing the distance between the probe and the sample accurately. In order to achieve this goal automatically and accurately, STM assistant automatic probe approaching pattern is adopted in XMU-BY-LG Scanning Electrochemical Workstation. So the first two steps are consistent with those in STM mode, i.e., approach the probe automatically to the surface of the sample through controlling the tunneling current.

The scanning principle of [Cl^-] probe: Using Pt microprobe to sense the tunnel current and Ag/AgCl microelectrode to sense the chloride ions concentration. There has triple function of the Pt microprobe: (a) to sense the tunnel current, precisely control the distance between the probe tip and the sample surface; (b) to measure the

in-situ STM image of the sample surface; (c) to serve as the reference electrode for the Ag/AgCl microelectrode, measure the concentration distribution of chloride ion in micro two-dimensional

1) Refer to Step (1) and (2) in STM Measurement (Notice: the [Cl^-] probe contains two micro probes. The Pt probe with a longer wire connects to the scanning wire during engage process, while another with a relative short wire is the Ag/AgCl microelectrode).

2) In STM mode, engage automatically until the voltage is less than 180V. Don't need for "Run single". After returning to the working interface, adjust the working mode to "Cl^- distribution", enter the intercept and slope of the serving probe, remember to press the "entre" key, then close the dialog box (Picture 3-17).



Picture 3-17 the interface of Cl^- distribution measurement

3) Choose “Function” menu---“Platform movement”. Move the platform upward for 500-1000 steps (50nm for every step). Close the dialog box after finish.

4) Exchange the probe connection. Remove the scanning probe connection from the Pt microprobe to the Ag/AgCl microelectrode (the shorter wiring), and connect the Pt microprobe (the longer wiring) to the reference probe connection.

5) Set the scanning parameters in the System setting window, such as the scanning direction, range, frequency etc..

6) You are suggested to choose “Background rejection” and set magnified times in the Signal parameter setting window to 100-200 times.

7) Add the research solution on the sample surface, then begin scanning.

8) After the completion of experiment, withdraw the probe.

9) Take off the probes and rinse the tips. Turn off the working software, controller and host successively.

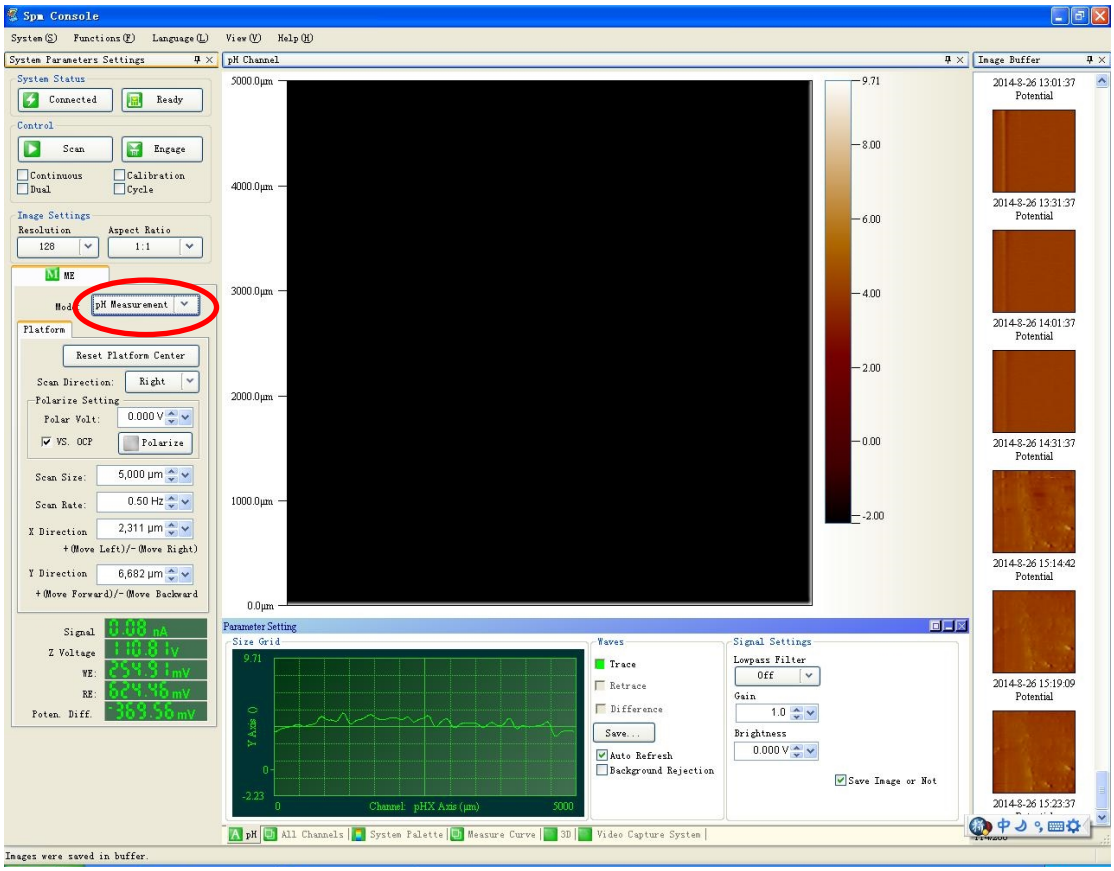
7. Micro-pH value Measurements (pH Distribution)

pH distribution still requires fixing the distance between the probe and the sample accurately. In order to achieve this goal automatically and accurately, STM assistant automatic probe approaching pattern is adopted in XMU-BY-LG Scanning Electrochemical Workstation. So the first two steps are consistent with those in STM mode, i.e., approach the probe automatically to the surface of the sample through controlling the tunneling current.

The scanning principle of pH probe：Using Pt microprobe to sense the tunnel current and W/WO_3 microelectrode to sense the hydrogen ions concentration. There has triple function of the Pt microprobe: (a) to sense the tunnel current, precisely control the distance between probe tip and the sample surface; (b) to measure the *in-situ* STM image of the sample surface; (c) to serve as the reference electrode for the W/WO_3 microelectrode, measure the concentration distribution of hydrogen ion in micro two-dimensional

1) Refer to Step (1) and (2) in STM Measurement (Notice: the pH probe contains two micro probes. The Pt probe with a longer wire connects to the scanning wire during engage process, while another with a relative short wire is the W/WO_3 microelectrode).

2) In STM mode, engage automatically until the voltage is less than 180V. Don't need for "Run single". After returning to the working interface, adjust the working mode to "pH distribution", enter the intercept and slope of the serving probe, remember to press the "entre" key, then close the dialog box (Picture 3-18).



Picture 3-18 the interface of pH distribution measurement

3) Choose “Function” menu---“Platform movement”. Move the platform upward for 500-1000 steps (50nm for every step). Close the dialog box after finish.

4) Exchange the probe connection. Remove the scanning probe connection from the Pt microprobe to the W/WO_3 microelectrode (the shorter wiring), and connect the Pt microprobe (the longer wiring) to the reference probe connection.

5) Set the scanning parameters in the System setting window, such as the scanning direction, range, frequency etc..

6) You are suggested to choose “Background rejection” and set magnified times in the Signal parameter setting window to 100-200 times.

7) Add the research solution on the sample surface, and then begin scanning.

8) After the completion of experiment, withdraw the probe.

9) Take off the probes and rinse the tip. Turn off the working software, controller and host successively.