Application of local electrochemical probes for energy studies

13/01/15

Introduction

Usual electrochemical techniques used to study the efficiency and properties of materials used in energy devices (fuel cells, batteries, solar cells) are potentio-, galvanostatic polarizations and electrochemical impedance spectroscopy (EIS).

Repeated polarizations with defined limits allow to investigate the capacity of the electrode and its evolution with time while EIS gives the evolution of the electrochemical mechanisms involved during cycling of the battery materials.

These techniques give a global response of the sample but further insights may be needed to actually identify and understand the specific mechanism responsible for increase or degradation of the electrode properties.

In this regard local probes give spatial insights at the microscale and allows to relate electrochemical behaviour with morphological properties..

A general knowledge of each the local probes is required.

Enjoy !

Outline

1. Fuel Cells

2. Solar Cells

3. Batteries

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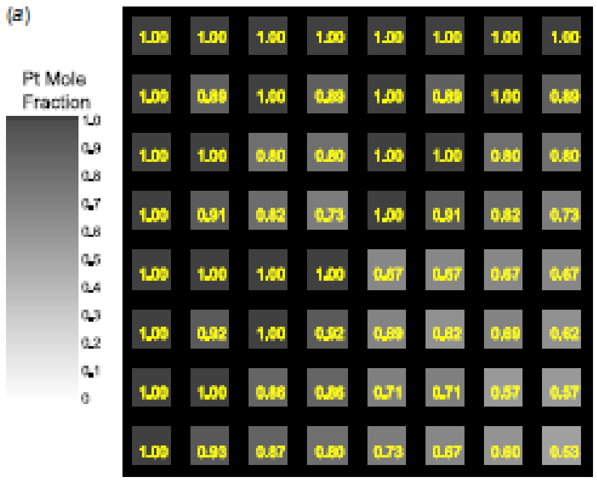
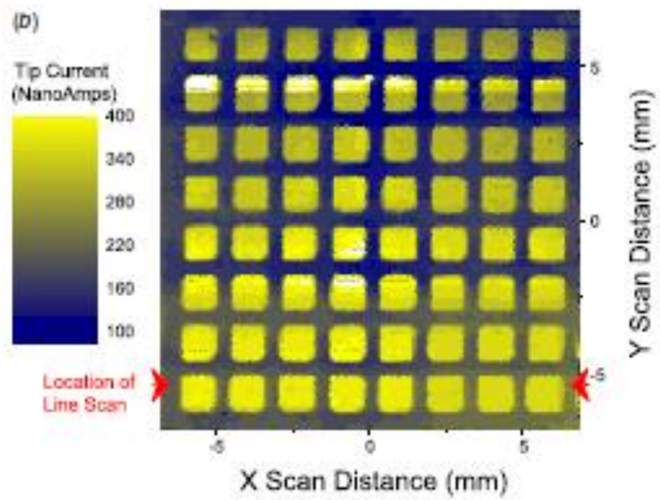
Fuel Cells - SECM

Uniscan SECM is used to study the the catalytic properties of Pt–Ru combinatorial libraries used as anode materials.

Arrays of Pt-Ru squares of different compositions are sputtered onto Si wafers.

SECM provides the change of conductivities as a fonction of composition.





PVD is used to produce arrays.

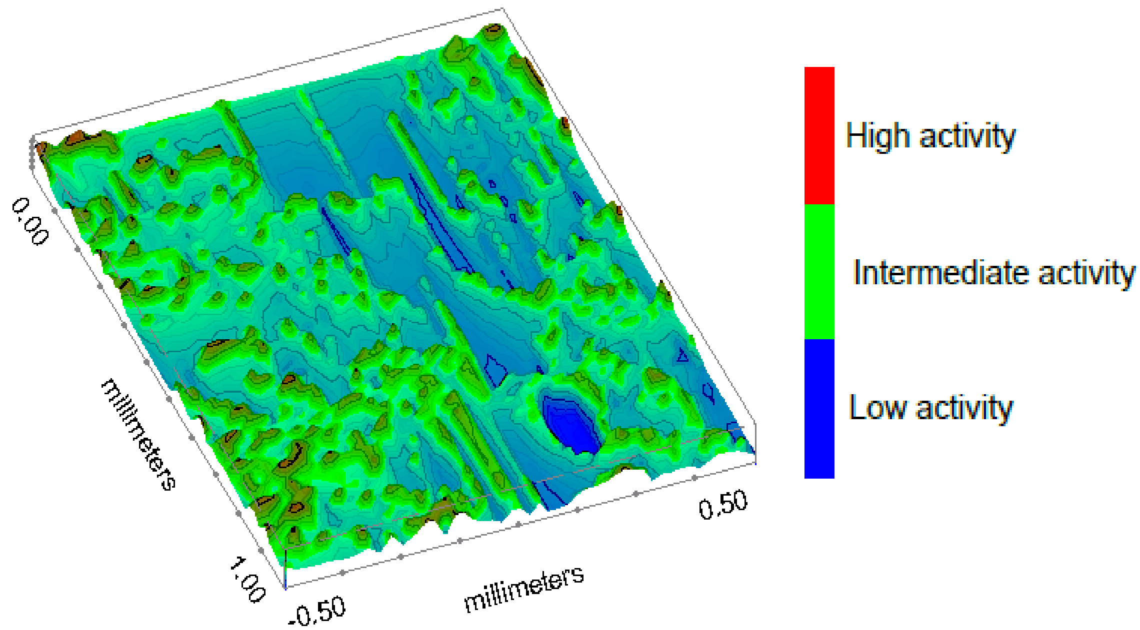
The electrolyte is H_2SO_4/Na_2SO_4.
The studied reaction is the proton reduction. SECM is used in G/C mode.

50/50 Pt/Ru was found to be the most active composition.

M. Black, J. Cooper, P. McGinn, Measurement Science Technology, 16, 2005, pp 174-182

Fuel Cells - SECM

Uniscan SECM was also used to study the microscale reactivity of a commercial JM Pt/C cast-film on HOPG.

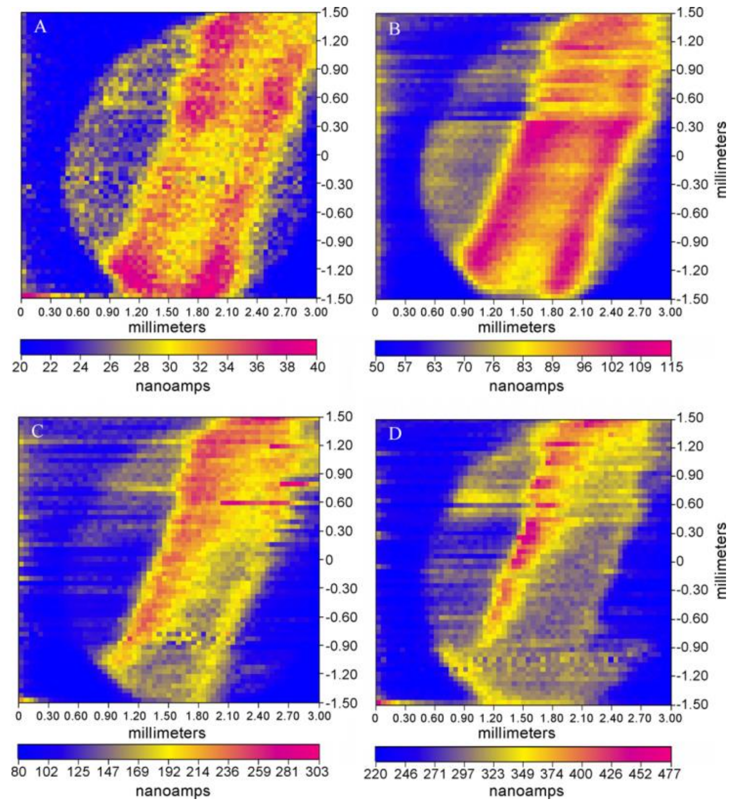


SECM map obtained in 5 mM H_2SO_4.

M. Williams, Master Thesis, University of Western Cape, 2005

Fuel Cells - SECM

Uniscan SECM in Tip Generation/Substrate Collection mode can be used for the study of ORR, for example on Pt thin films.



Pt stripe in 0.5M H_2SO_4 for different substrate potentials.

G. Lu, J. S. Cooper, P. J. McGinn, Electrochimica Acta 52 (2007) 5172–5181

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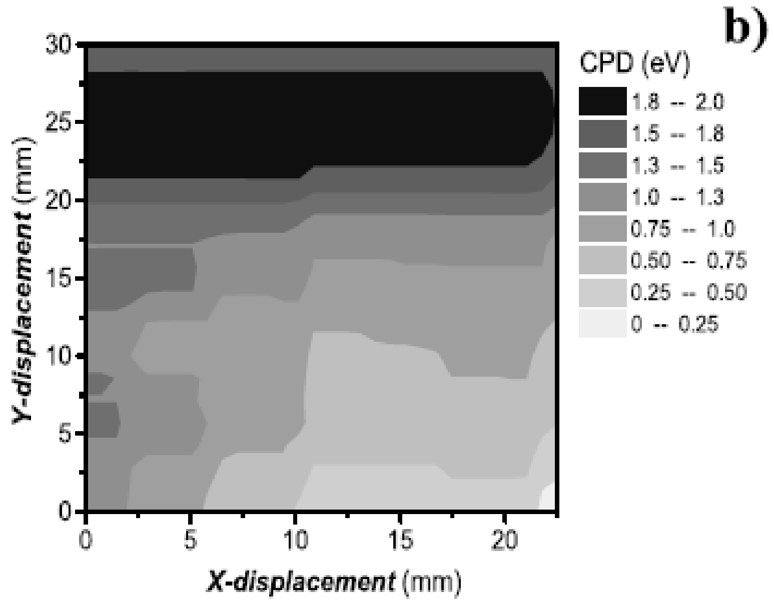
Solar Cells - SKP

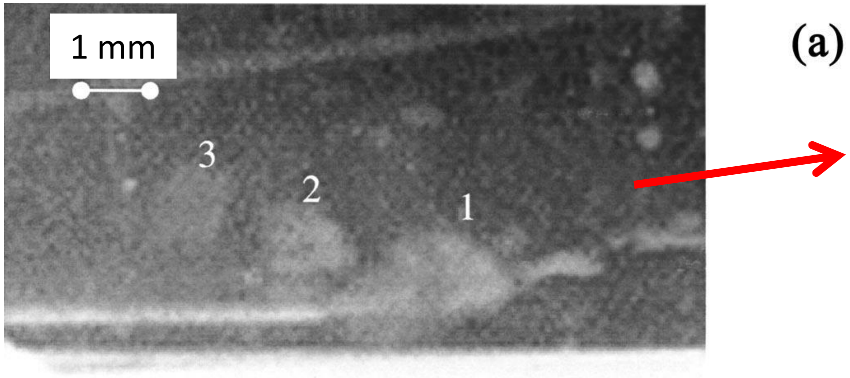
Uniscan SKP is used to characterize semiconductor materials and detect contaminants.



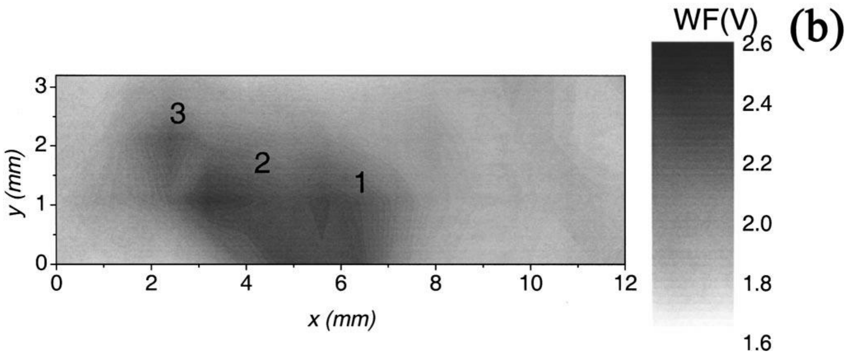
Contact Potential (or Work Function) Difference map of a multicrystalline Si, B-doped, NaOH etched wafer.
CPD response depends on the presence of contaminants on the surface and can be used to characterize the cleanliness of semiconductors.

A. Castaldini, D. Cavalcoli , A. Cavallini, M. Rossi, Materials Science and Engineering B91–92 (2002) 234–238

Uniscan SKP is used to detect contaminants.



Optical microscope picture

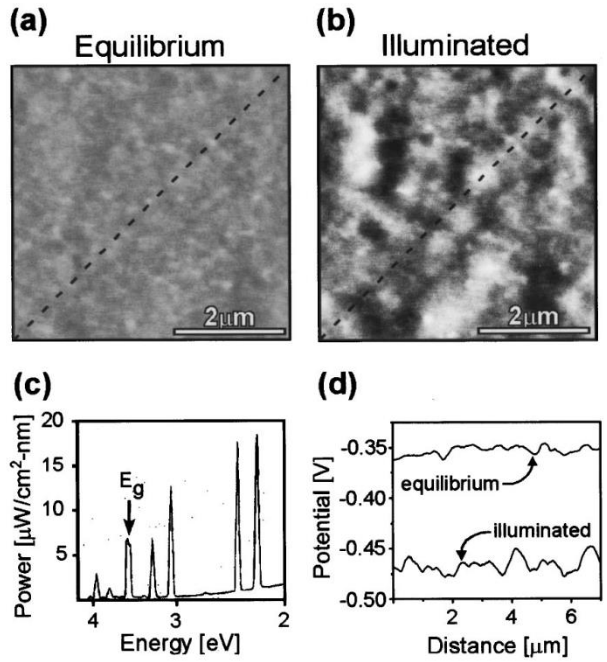


Contaminants correspond to a contrast in WF maps.

D. Cavalcoli, A. Cavallini, M. Rossi, S. Binetti, F. Izzi and S. Pizzinia, J. Electrochem. Soc., 150 G456-G460 2003

Solar Cells - SKP

SKP is used to characterize semiconductor materials under illumination.



SKP area maps and line scans of p-type GaN w/o and under illumination.
Illumination reduces the overall surface potential and increases the magnitude of surface potential variations.
Darker areas are due to a higher density of dislocations.

B. S. Simpkins, E. T. Yua, U. Chowdhury, M. M. Wong, T. G. Zhu, D. W. Yoo, and R. D. Dupuis, Journal of Applied Physics, vol. 95, 11 1, 2004 p. 6225

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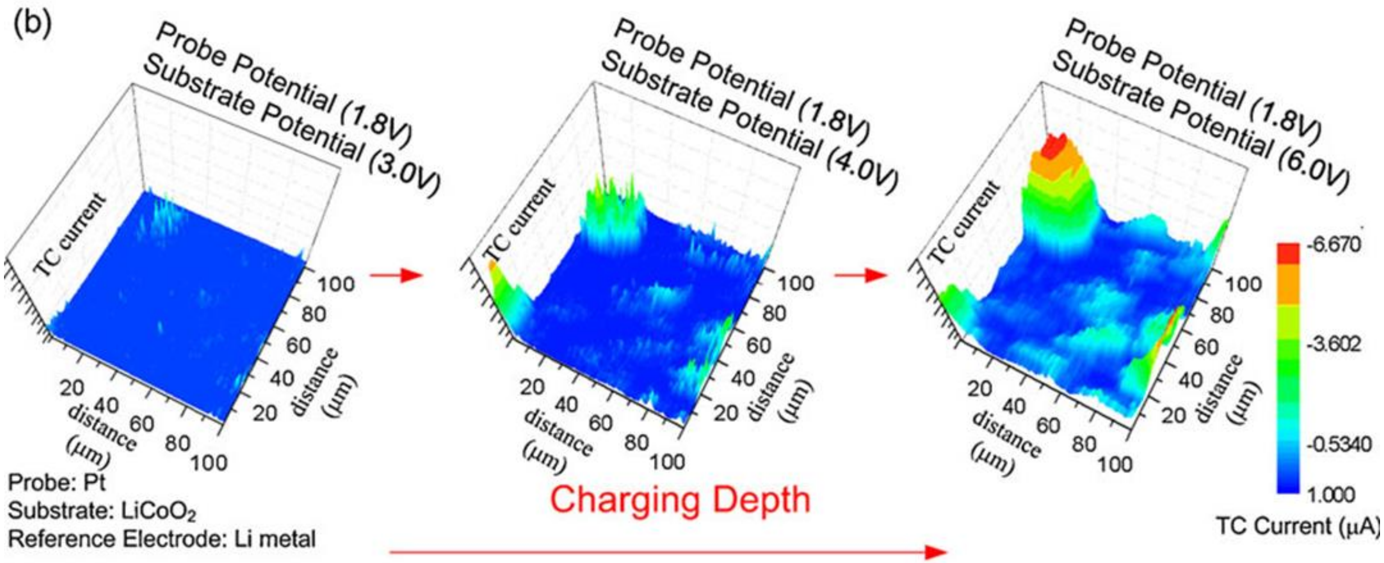
Batteries - SECM

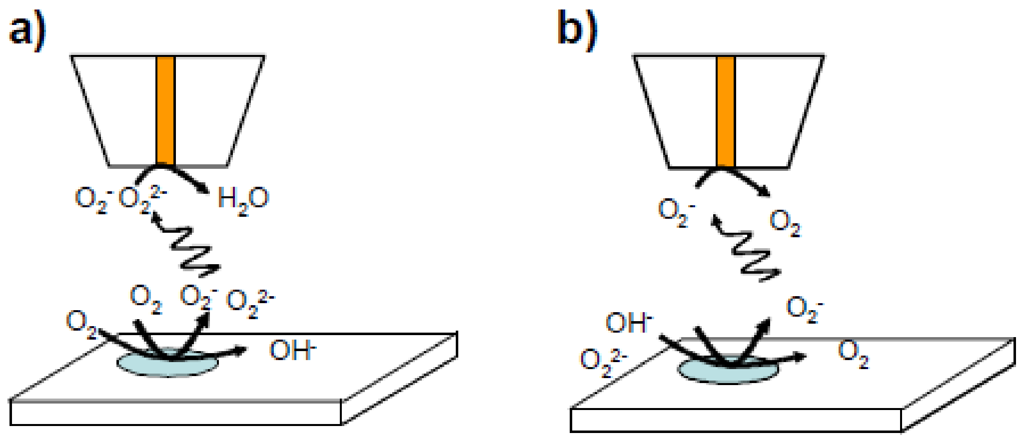
SECM is used in SG/TC mode to study the Li^+ dissociation from LiCoO2 electrode.



SECM shows non-uniformity of the LiCoO2 distribution.

F. Xu, B. Beak, C. Jung, J Solid State Electrochem (2012) 16:305–311

Study of the air electrochemical reaction (oxygen reaction, oxygen production) at the positive electrode (Zn) of the Air-Zn secondary battery.



The electrolytes are aqueous alkaline solution, protic ionic liquid, aprotic ionic liquid and ionic liquid mixtures with water in different ratio.
The influence of the deposition of discharging product (ZnO) and carbonate (by-product in alkaline electrolyte) to the functioning of the gas diffusion electrode are also investigated.

A. L. Gui, G. Wittstock, Abstract #535, 224th ECS Meeting, 2013 The Electrochemical Society

Study of oxygen evolution on NiOH electrode used in Ni-based supercapacitor.
Two concurrent reactions are involved in the charging of NiOH electrode :

$$NiOH_2 + OH^- \leftrightarrow NiOOH + H_2O + e^-$$
$$4OH^- \leftrightarrow O_2 + 2H_2O + 4e^-$$

SECM is used in SG/TC to determine the onset potential of O_2 generation.

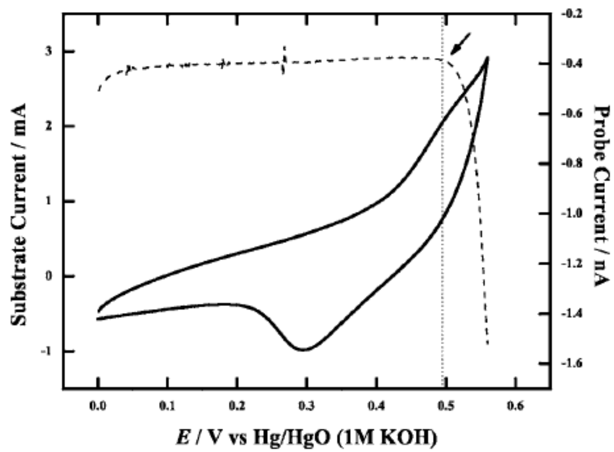


Figure 5. SG-TC SECM measurements (— CV, --- probe current) of 100 μm coating of nickel hydroxide (type A) standard mix (active material, graphite, and binder) on 20 μm nickel foil at a scan rate of 2 mV s^{-1}. The arrow indicates the point of oxygen detection at the probe tip.

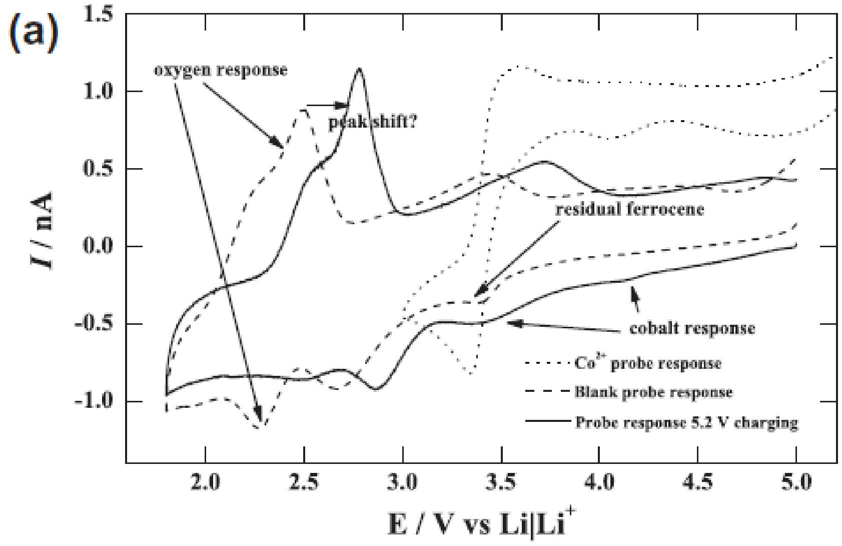
The effect of additives on the ability for $Ni(OH)_2$ electrodes to produce O_2 can be estimated.

Batteries - SECM

Study of dissolution of $LiCoO_2$ in ionic liquid.

CV's are performed on the 10 µm tip (50 mV/s) to detect dissolved species from the LiCoO2 electrode.

MUST BE INSTALLED IN A GLOVE BOX



Cyclic voltammogram of the Pt (10 lm) microelectrode probe tip in C4mpyrTFSI at 50 mV s-1, showing the effect of overcharging by utilising a bias potential of 5.2 V vs Li|Li+

It was found that the majority of the degradation of the cathode material occurs during deep discharge.

G. A. Snook, T. D. Huynh, A. F. Hollenkamp, A. S. Best, J. Electroanal. Chem. 687 (2012) 30–34

Batteries - SECM

Study of Li+ intercalation into graphite using a metallic Li UME.
Li^+ is generated at the tip and collected/intercalated by/into the graphite substrate.

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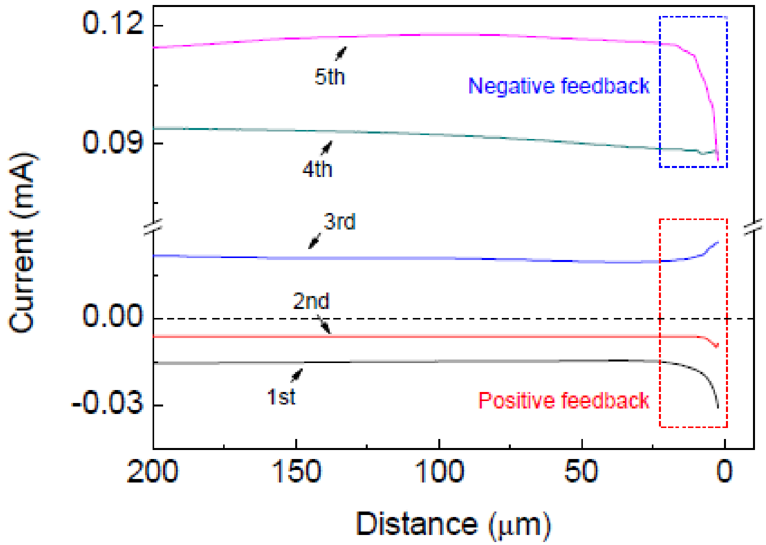

Figure 1. Current profiles measured by PSC technique. (potential conditions are 0.0V for Li metal tip and 4.0V for Pt electrode)

So far only approach curves were studied.

F. Xu, C. Jung, IMLB 2010 Proceedings

Useful links

More references can be found here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/references/coatings/

Please also find some application notes here :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/application-notes/

And the brochures here :
http://www.bio-logic.info/scanning-systems-scan-lab/downloads/brochures/

Requests can be placed here :
http://www.bio-logic.info/ask-for-a-quote-contact-us/

For more information on the techniques :
http://www.bio-logic.info/scanning-systems-scan-lab/scan-lab-literature/tutorials/