# Can electron tunneling occur in a hundred-nanometer thick Nafion film and be utilized to image Nafion/electrode interfaces with an angstrom level resolution?

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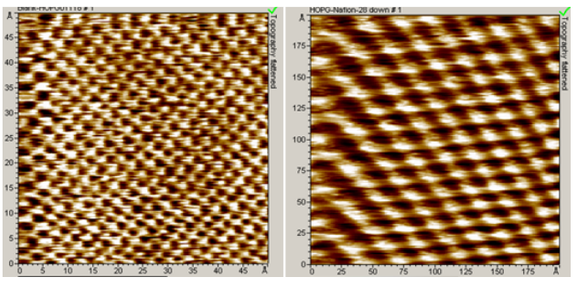
Scanning tunneling microscopy (STM) usually can only penetrate a surface film of a few angstroms. In the present study STM was used to investigate HOPG and Pt samples coated with a recast hundred-nanometer thick Nafion film. Ag is painted on the film as the counter and Ag|AgCl strip as the reference electrode to form an all-solid-state electrochemical cell.

Fig. 1 clearly shows that the spacing between the atoms was approximately 2.5 Å on the blank HOPG, which was in good agreement with what was previously observed for blank HOPG. For the Nafion-coated HOPG sample, the image also shows a periodic pattern with a similar symmetry but with a greater spacing (10-20 Å). Fig. 5 shows the three most recorded patterns from the Nafion-coated samples: triangular nets, diamond arrays, and honeycomb nets. The spacings between atoms for these patterns are 10-25 Å.



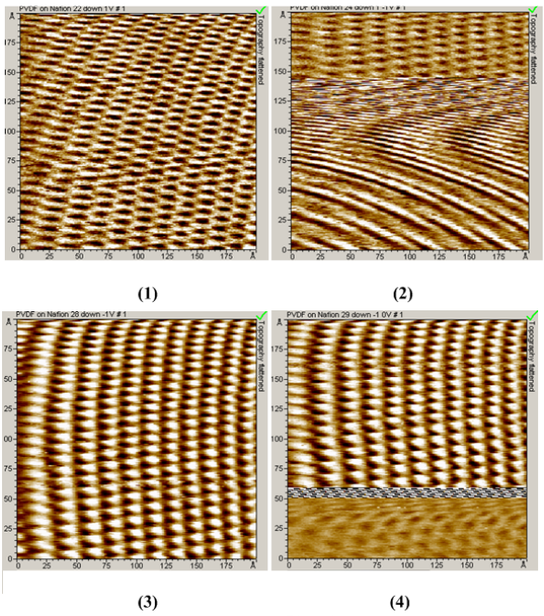
**(1)** **(2)**

Fig. 1. STM topographic images of the HOPG samples: (1) A blank HOPG piece, and (2) an HOPG piece coated with a Nafion film (bias: -0.4V, set current: 0.2 nA).

Fig. 2 shows the responses of the images to changes in the applied potential. Fig. 2(1) shows an image obtained for the initial applied potential of 1.0 V. When the applied potential was switched from 1.0 to -1.0 V, the periodic arrays (a deformed honeycomb net) disappeared immediately. Then, after a few minutes, a different type of periodic array (with triangular shapes) appeared. When the applied potential was switched back to 1.0 V, the periodic arrays with the triangular shapes disappeared, and the hexagonal net reappeared. These results were repeated several times.

The following conclusions can be made based on the present study:

1) Images with atomic resolution can be obtained with an STM on electronically conducting substrates coated with a 100-500 nm thick Nafion film.
2) The images obtained from the Nafion-coated samples reflect the structures of the interfaces between the Nafion film and the substrates.
3) Highly ordered patterns were obtained from coated HOPG samples, and the patterns were altered by changing the potential of the HOPG substrate. The spacings of the periodic arrays of atoms on the Nafion-coated samples were much larger than those observed on blank samples.
4) Online visualization of the changes upon changing the electrochemical potential of the substrate can be realized with this method.
5) The proposed theory of electron resonant tunneling explains the observations well.



**(1)** **(2)** **(3)** **(4)**

Fig. 2. The response of the STM image to changes in the applied potential: (1) at 1.0 V, (2) switching from 1.0 to -1.0 V, (3) at -1.0 V, (4) switching from -1.0 to 1.0 V.