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Na_xCoO_2: A New Opportunity for Rewritable Media?

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Investigations of the layered cobalt oxide series have yielded several solids exhibiting interesting physical properties and have also led to materials of considerable technological significance.[1] Na_xCoO_2[2], exhibiting interesting electrochemical properties[3] related to sodium intercalation/deintercalation processes, is attracting a renewed current interest due to the recent observation of its large thermoelectric power[4] and the superconductivity of $Na_{0.3}CoO_2$ intercalated with water.[5]

As part of our continuing conducting probe (CP)-AFM studies,[6] our present objective is to develop probe-mediated electrochemical local surface modifications that can be controllably reversed. Electrochemical scanning-probe lithography methods involve instruments (STM or CP-AFM) operating in the so-called scanning electrochemical microscopy (SECM) mode.[7] CP-AFM uniquely allows the simultaneous investigation of the surface topography and the transport properties of solids, the topographical imaging being controlled solely by contact forces, independently of the voltage required for the transport measurements. In contrast, the STM method involves inescapable height-to-current interdependence in the tunnel−current range.[8] Up to now, AFM-mediated approaches[9] have been investigated for reversible nanometer-scale surface patterning, with a view to scanning-probe-mediated data storage applications. Several irreversible surface modifications have been investigated by AFM, but reversible ones are scarce. Thermomechanical writing,[10] ferroelectric thin-film polarization switching,[11] and organic thin-film conductance switching[12] have been examined, but no results on reversible electrochemical surface patterning by CP-AFM have yet been reported. A prerequisite in achieving this goal is the availability of a solid exhibiting several stable redox stages associated with reversible structural changes. We decided to investigate Na_xCoO_2[13] as a candidate material.

We here report that the surface conductivity of Na_xCoO_2 ($x = 0.79$) can be reversibly modified by CP-AFM. These electrochemically reversible surface modifications indicate the potential of these materials as nanoscale rewritable media.

The surface modifications of a single crystal of Na_xCoO_2[14] by a CP-AFM operated under a dry nitrogen flux[14] are summarized in Figure 1 (images recorded at +1 V bias voltage). For positive (oxidative) patterning bias (+2.5 V) and in striking contrast to all previous AFM probe-induced local surface oxidations,[6a,15] which have exclusively produced insulating regions, a more conductive area than the starting crystal surface is now obtained. The surface modifications are not symmetrical; adjusting the patterning bias to a negative value (−2.5 V) yields the formation of an insulating region. This excludes mechanical and/or electric field effects as sources of these modifications and indicates electrochemical reactions occurring within the condensation water capillary meniscus nanocell at the probe−substrate contact (the faradic part of the current being maintained, as usual, by coupling to water redox reactions occurring on the tip).[6a,7a,b] The electrochemical origin of these modifications is also confirmed by the current/potential curves exhibiting a spectacular dissimilarity as a function of the potential scan direction (Figure 2).

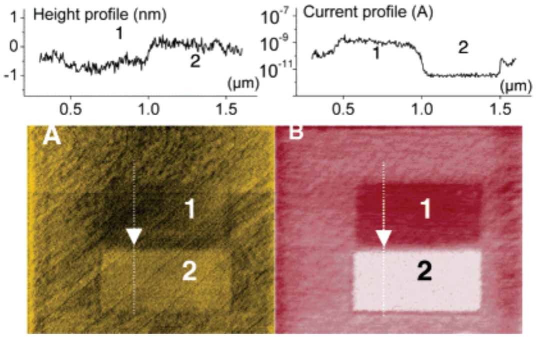

Figure 1. CP-AFM images of probe-mediated surface modifications of the *ab* face of a Na_xCoO_2 single crystal (the topography is shown in A, and the simultaneously recorded (at +1 V bias voltage) surface conductivity in B). For a 1 μm^2 surface modification, the upper half is first scanned with an anodic crystal bias (+2.5 V) and results in a more conducting region than the starting surface (see B1); the lower half of the 1 μm^2 area is scanned with the opposite tip−substrate bias (−2.5 V) and exhibits a more insulating area (see B2). It is also worth noting the corresponding topographic surface modifications (A).

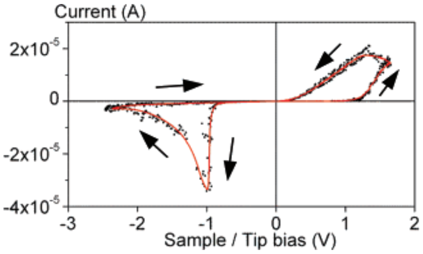

Figure 2. Tip−sample current−potential behavior of the *ab* face of a Na_xCoO_2 single crystal. The scan in the positive potential range highlights an increased conductivity, whereas in the negative direction, the current is interrupted by formation of an insulator.

Whenever electron exchange reactions of Na_xCoO_2 occur, the coincident occurrence of intercalation/deintercalation of sodium is well established.[3,16] The control of electronic properties of these solids by the redox state (indicated[17] by the sodium content) is also

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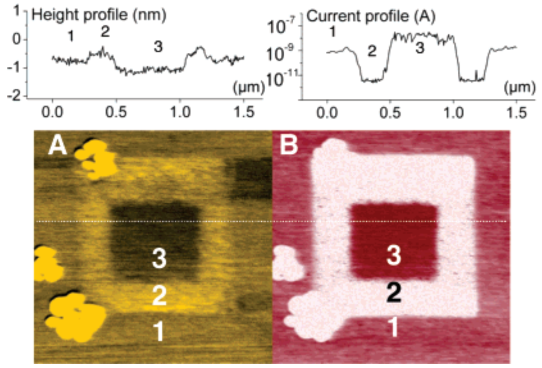

Figure 3. CP-AFM images (recorded at +1 V bias voltage) of probe-mediated surface modifications of the *ab* face of a Na_xCoO_2 single crystal showing the reversibility of the process (the three outgrown insulating spots are not related to the probe-mediated modifications).[14] A first 2 × 2 μm^2 scan with an oxidative +2.5 V substrate−tip bias generates a more conductive region (see B1); then, a 1 × 1 μm^2 scan within this modified region using the opposite tip−substrate bias (−2.5 V) yields an insulating area (B2). A subsequent 0.5 × 0.5 μm^2 scan with the first tip−substrate bias (+2.5 V) restores back the conducting area (B3).

well documented.[22] Thus, a decrease in *x* (from 0.75 to 0.31)—reflecting deintercalation of sodium by an oxidative process—results in a significant increase in Na_xCoO_2 conductivity.[22] It might therefore be reasonably assumed that our AFM-mediated electrochemical surface modification, yielding more conductive areas for a positive (oxidative) bias (Figure 1B, 1), corresponds to a similar sodium deintercalation process. Conversely, the surface modification obtained with the opposite (negative) bias, yielding a more insulating region (Figure 1B, 2), corresponds to a sodium intercalation (reduction). These stable modifications therefore reflect confined redox processes of the cobalt oxide lattice, resulting simultaneously in formation of local concentration gradients of the sodium counterions. Moreover, this assumption is reinforced by the corresponding topographic images (in Figures 1A and 2A) reflecting significant modifications of the *c*-axis parameter, as might be expected[16,19,22] for electrochemical processes involving modification of the sodium content *x* of Na_xCoO_2.

The reversibility of these surface conductivity modifications[23] has been investigated, and the results are illustrated in Figure 3 (images recorded at +1 V bias voltage). A more conducting 2 × 2 μm^2 area is first created by an oxidative +2.5 V scan (Figure 3B, 1), then a 1 × 1 μm^2 insulating region is created within this area by a second patterning scan at −2.5 V (Figure 3B, 2). A subsequent scan (0.5 × 0.5 μm^2) within this newly formed insulating area with a positively biased tip (+2.5 V)[24] yields again a conducting region (Figure 3B, 3).

In summary, these preliminary results show that the Na_xCoO_2 single-crystal surface can be conveniently modified by conducting-probe-mediated reversible electrochemical sodium intercalation/deintercalation reactions; the process yields more conducting (or more insulating) patterns, with versatile erasing. This electrochemical procedure also opens the way to possible nanoscale modifications of alternative layered materials by probe-mediated intercalation/deintercalation reactions, which might in turn lead to an extension of the well-documented dip-pen nanolithographic methods.[25] Work is in progress in our laboratories to develop the scope and potentialities of this approach.

Supporting Information Available: Experimental details on the materials and samples preparations, electrochemical impedance spectroscopy measurements and instrumentation; CP-AFM images of the initial freshly cleaved Na_xCoO_2 single-crystal surface, and the irreversible probe-mediated surface modifications obtained by an increase in the probe/substrate potential bias to +3 V. This material is available free of charge via the Internet at http://www.pubs.acs.org.

Note Added after ASAP Publication. Corrections were made in the Figure 1 caption on May 31, 2007.

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(24) The value of the sodium content *x* reached after such a back-and-forth intercalation/deintercalation process (and consequently the surface conductivity) is not necessarily equal to the starting *x* value (compare the electrical profiles in Figure 3B, 1 and 3).
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