Electrochemical Reactivity of Carbon Monoxide and Sulfur Adsorbed on Ni(111) and Ni(110) in a Lithium-Based Solid Polymer Electrolyte in Ultrahigh Vacuum

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The effects of adsorbed carbon monoxide and sulfur on the electrochemical properties of Ni(111) and Ni(110) in $LiClO_4$−poly(ethylene oxide) (PEO) solutions have been examined by cyclic voltammetry at a temperature of 333 K in ultrahigh vacuum (UHV) environments. Rather sharp peaks were found in the first scan in the negative direction for $c(4 \times 2)$CO and sulfur overlayers on Ni(111) centered at 0.5 and 1.25 V, respectively. In contrast, the voltammetric features observed in similar experiments for Ni(110) exposed to 30 L of CO and for Ni(110)−$c(2 \times 2)$S were broad and not as well defined. These processes are attributed to reactions between Li underpotential deposition (UPD) and CO and sulfur overlayers to yield, correspondingly, Li_2O (and a polymeric Li−CO adduct) and Li_2S as the most likely products.

Introduction

In the course of a study aimed at examining various aspects of lithium underpotential and bulk deposition on Ni(111) from $LiClO_4$(PEO) solutions in ultrahigh vacuum (UHV), a sharp peak was observed during the first linear scan in the negative direction centered at 0.5 V vs a Li counter reference electrode, Li[C/R], and ascribed tentatively to the presence of adventitious CO adsorbed on nickel.[1]

This paper provides a more detailed description of this interesting phenomenon employing CO-modified Ni(111) and Ni(110) surfaces prepared under better controlled conditions. Also to be discussed are the effects of sulfur, an impurity often found in bulk nickel, on the voltammetric characteristics of the same two *nominally* clean Ni single-crystal substrates. Unlike other common, relatively inert electrode materials such as gold, silver, and platinum, nickel does not form alloys with lithium at room temperature[2] and, therefore, affords unique properties for fundamental electrochemical studies of this highly reactive metal.[1,3]

Experimental Section

All measurements were carried out in a custom-made UHV chamber (Perkin-Elmer, base pressure of 2×10^{-10} Torr) equipped with low-energy electron diffraction (LEED) optics (PHI 15-120) and a hemispherical energy analyzer (VSW) for Auger electron spectroscopy (AES).[4] The Ni(111) and Ni(110) crystals used in this study (Cornell Laboratory) were circular disks of ca. 0.8 and 1 cm^2 cross sectional area, respectively, oriented to ~1° by Laue back-diffraction, mounted on transferable holders.[5] Specimens were cleaned by Ar^+-sputtering (0.5−1.5 keV)/thermal-annealing (850−1175 K) cycles, using resistive heating, and characterized by AES and LEED. A K-type thermocouple spot-welded to the edge of the crystals was used to monitor the temperature.

Carbon monoxide was adsorbed on clean nickel surfaces by exposure to 30 L of CO in UHV at room temperature. In the

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case of Ni(111), a sharp LEED pattern was observed that was consistent with a $c(4 \times 2)$CO superstructure, in agreement with data reported in the literature.[6−12] Also in accordance with information published elsewhere[13] was the increase in the background intensity of the rectangular Ni(110) LEED pattern following dosing, attributed to the presence of an amorphous CO overlayer. No AES spectra or LEED patterns were recorded after CO adsorption prior to the electrochemical experiments, to avoid electron-induced decomposition.[14]

Sulfur-modified nickel surfaces were obtained by simply annealing the specimens to a high enough temperature to induce surface segregation.[15,16] Clean Ni(110) surfaces heated at ca. 1070 K for several hours yielded AES spectra displaying, in addition to Ni features, a prominent S peak (19% by AES), without additional contributions due to other elements, and LEED patterns showing additional center spots on the basic rectangular array resembling a distorted hexagonal lattice. These latter results are in harmony with earlier LEED reports by Demuth and Rhodin[15] and with more recent UHV-STM findings by Backer and Horz,[16] who describe this superstructure as a $c(2 \times 2)$S, suggesting that the sulfur atoms are chemisorbed in 2-fold hollow sites on Ni(110). Extensive annealing of clean Ni(111) in UHV was also found to yield significant amounts of sulfur (14% by AES) and an increased background in the LEED pattern; however, none of the various ordered superstructures observed by LEED[15] (or UHV-STM[16−19]) upon dosing Ni(111) with H_2S in UHV could be readily discerned.

Electrochemical experiments were performed in $LiClO_4$(PEO) electrolytes in UHV at temperatures of ca. 60 °C, using instruments and procedures described in detail in ref 20 and other publications cited therein.

Results and Discussion

1. CO-Modified Single-Crystal Nickel Surfaces. *A. Ni(111).* As briefly mentioned in the Introduction, the first voltammetric cycle of *nominally* bare Ni(111) in pre-electrolyzed $LiClO_4$(PEO) at 333 K at a scan rate of 5 mV/s was reproduced for completeness in panel A of Figure 1(solid line), displayed
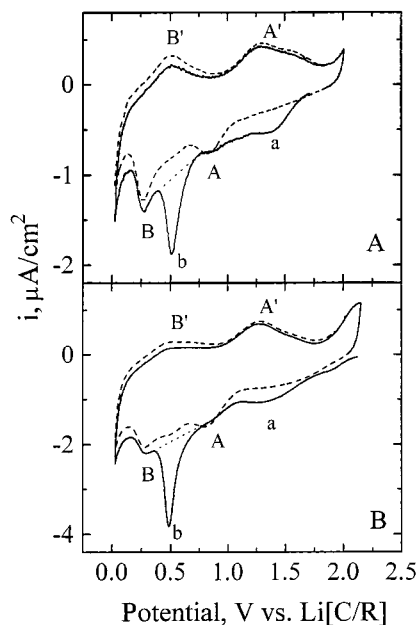
Figure 1. First (solid line) and second (dashed line) voltammetric cycles for a nominally clean Ni(111) (panel A) and Ni(111)−c(4× 2)-CO surfaces (panel B) in LiClO$_4$−PEO at 333 K. Scan rate was 5 mV/s. The somewhat arbitrary baseline used for the Coulometric analysis of peak b is shown as dotted lines.

a rather prominent peak, b, in the scan in the negative direction, which disappeared in the second (dashed line in this panel) and subsequent cycles.[1] This feature was attributed to the presence of adventitious CO in the main UHV chamber (<1 × 10^{-10} Torr), which adsorbed on Ni(111) during the rather long time (ca. 1 h) required for the specimen to cool to ca. 333 K, following flash thermal annealing, and for the cell to be transferred into the main UHV chamber. This assignment could be further confirmed in this work by exposing clean Ni(111) to CO to form a stable c(4 × 2)CO superstructure (see Experimental Section), for which the first linear scan yielded a more pronounced peak b (solid line, panel B of Figure 1). The potential at which this feature occurs is sufficiently negative for lithium to underpotential deposit on Ni, as evidenced by the two sets complementary peaks A,A′ and B,B′ shown more clearly in the second scan (dotted line);[1] hence, it seems reasonable to assume that the effect observed is derived from interactions between coadsorbed (underpotential deposition, UPD) Li and CO on the surface.

Support for this view is provided by the work of Jaensch et al.,[21,22] who examined Li−CO coadsorption on Ru(001) and Ag/Ru(001). On the basis of temperature-programmed desorption (TPD), work function, and metastable quenching (MSQ) electron emission spectroscopic techniques, these authors concluded that coadsorbed CO and Li interact to generate, depending on the surface stoichiometry and temperature (*T*), at least two different species. In particular, for small Li coverages and at low substrate temperatures (80 K), a Li−CO complex with stoichiometry Li$_n$(CO)$_{2n}$ appears to form, which undergoes decomposition at $T > 750$ K. The TPD of CO exposed to Li-modified Ru(001) at 400 K was consistent with Li$_2$O and the polymeric Li−CO complex as being the most likely products; it seems, therefore, plausible that the same species are produced by the reaction between UPD Li and preadsorbed CO in the electrochemical experiments. Unfortunately, both the amount of reactive Li on the surface and the stoichiometry of the species produced are not known with certainty; hence, no reliable information can be obtained from a simple Coulometric analysis.
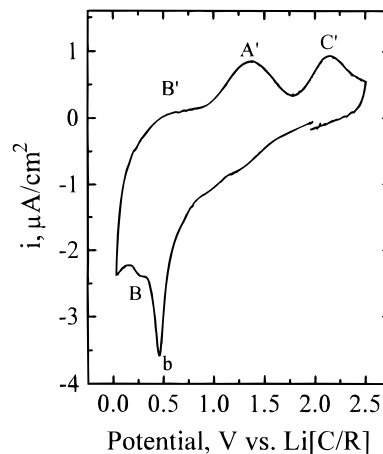

Figure 2. Same as for panel B of Figure 1 under extremely clean conditions. Note the presence of a well-defined peak C′ (see text for details).

Nevertheless, it is significant that the charge under peak b, using a rather arbitrary baseline (see dotted lines in panels A and B of Figure 1), increases by about a factor of 2 for Ni(111)−c(4 × 2)CO surfaces (41 μC/cm^2) compared to CO-contaminated Ni(111) (20 μC/cm^2), for which the amount of CO would be expected to be smaller. Furthermore, the atomic density for Ni(111) is 1.86 × 10^{15} atoms/cm^2, which is equivalent to a charge density of ca. 300 μC/cm^2, assuming one electron per surface atom. Within the uncertainties in the electrode area and considering that the coverage of CO for a c(4 × 2) superstructure is $^1/_2$, the charge associated with peak b in panel B of Figure 1 would correspond to about 0.3 electrons per CO molecule.

The disappearance of peak b in the second and subsequent cycles would be consistent with the irreversible formation of a superficial layer of Li$_2$O, an electrochemically inert material that would consume oxygen from CO, leaving the remaining carbon in a yet to be identified state. Another aspect of these results that requires further investigation is the presence of a peak with an onset potential of ca. 1.8 V observed during the first and subsequent scans in the positive direction upon reversal of the scan at 0.05 V. As shown by the results obtained for a very clean Ni(111)−c(4 × 2)CO surface (no noticeable peak a) in Figure 2, this feature, denoted as C′, is centered at about 2.1 V and thus is very close to that reported earlier for oxygen-modified Ni(poly) in the same media.[1] Whether the oxygen in this case is derived from monomeric or polymeric CO of the type proposed by Jaensch et al.[21,22] (vide supra) or from the reduction of PEO or perchlorate ion still remains to be explored.

B. Ni(110). Further insight into a possible surface-specific character of coadsorbed Li−CO interactions on Ni was sought by conducting identical electrochemical experiments on Ni(110). As shown in panel A of Figure 3, the first scan in the negative direction (solid line) for a *nominally* clean Ni(110) initiated at the open-circuit potential (ca. 1.8 V) yielded a very large feature consisting of at least three clearly identifiable peaks or shoulders. At least two of these peaks disappeared during the second (dashed line in this figure) and subsequent cycles, giving rise to two sets of complementary peaks (dotted and dash−dot curves in Figure 4), somewhat reminiscent of those found for Ni(111) after the first scan in the negative direction (Figure 1) and attributed to Li UPD. Evidence that the shoulder at 1.25 V in the first scan in the negative direction may be related to a process associated with the presence of CO was obtained from experiments in which Ni(110) was exposed to 30 L of CO, which, as shown in Panel B of Figure 3 (solid line), gave rise to a clearly
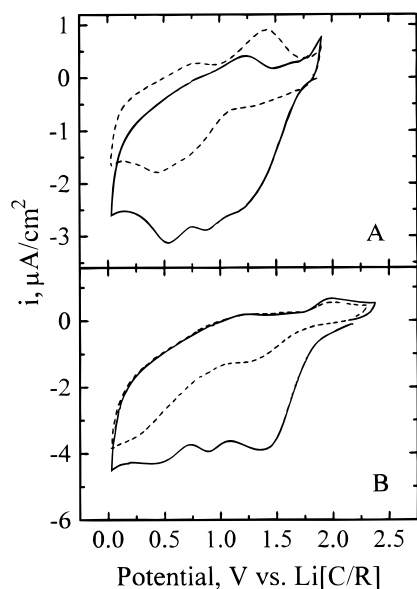
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Figure 3. First (solid line) and second (dashed line) voltammetric cycles of nominally clean Ni(110) (panel A) and Ni(110) exposed to 30 L of CO (panel B) in LiClO₄−PEO at 333 K. Scan rate was 5mV/s. The peak at the more positive potential attributed to reactions involving Li and CO appears to contain contributions due to sulfur (see text).
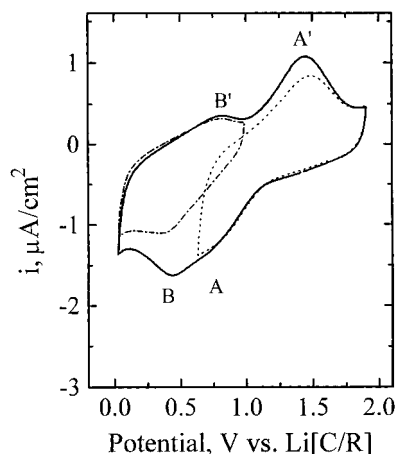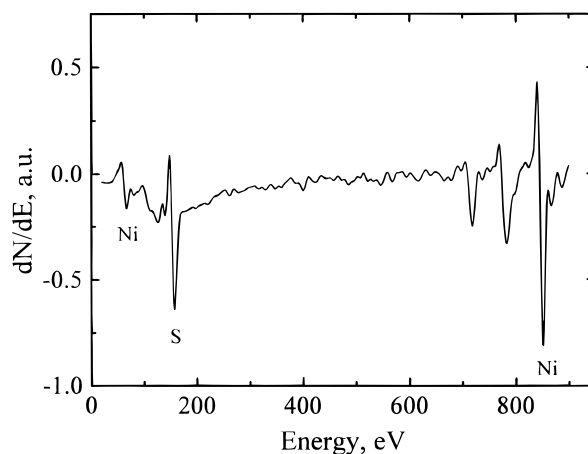

Figure 5. Auger electron spectrum of an extensively annealed Ni(111) surface showing a rather large amount of superficial sulfur (14%) (see Experimental Section for details).
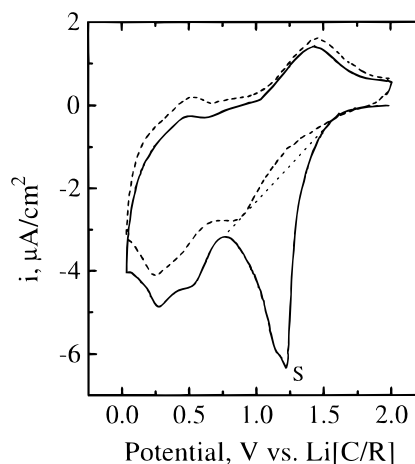

Figure 4. Steady-state voltammogram for the surface in panel A of Figure 3, showing the complementary of peaks A,A′ and B,B′. Other conditions are the same as those specified in Figure 1.

Figure 6. First (solid line) and second (dash line) voltammetric cycles of a sulfur-contaminated Ni(111) surface described in caption of Figure 5.

defined peak centered at about 1.4 V. Particularly striking is the very distorted character of the voltammogram obtained during the second (see dotted line in this panel) and subsequent scans, which may be indicative of irreversible changes on the surface induced at least in part by reactions between Li and CO. Also to be considered are the effects of sulfur to be discussed in the following section, which introduce yet additional complications to the interpretation of these data.

2. Sulfur-Modified Ni Single-Crystal Surface. *A. Ni(111).* Extensive annealing of fresh Ni(111) crystals was found to promote segregation of sulfur to the near-surface region as shown by the AES spectrum in Figure 5, without generating additional spots in the LEED pattern (see Experimental Section). A very distinct voltammetric peak at 1.25 V vs Li[C/R] could be found for these specimens during the first cycle (solid line, Figure 6), which, as in the case of CO, disappeared during the second cycle to yield a curve virtually identical to that obtained for *nominally* clean Ni(111) after the same treatment (dotted lines, Figure 1). It seems reasonable to suggest, from a chemical

viewpoint, that sulfur reacts with Li UPD to form an electrochemically inert Li−S surface layer, which, on the basis of the recent results obtained for S adsorbed on Li using soft X-ray photoemission, could be Li₂S.[23] In fact, the charge under the sulfur-induced voltammetric feature curve is about 247 μC/cm², which would correspond to close to 1 electron per surface site, or equivalently, 2 electrons per S atom on the surface, on the basis of the size of the AES S signal obtained for Ni(110)−c(2 × 2)S (vide infra) for which the coverage is one-half. It may be noted that the onset potential for this feature occurs at about the same value as that of peak a in Figure 1, suggesting that the latter may not be due to water, as was originally proposed,[1] but to small amounts of sulfur remaining on the surface after the cleaning procedure not detectable by AES under the measurement conditions.

B. Ni(110). In analogy with the behavior found for S-modified Ni(111), an additional feature of rather similar nature could be found for Ni(110)−c(2 × 2)S during the initial scan (solid line, panel A of Figure 7). Also shown in that figure (dotted line) is the subsequent voltammetric cycle. Further evidence for sulfur being responsible for this effect was obtained by placing the LiClO₄(PEO) film on an area adjacent, although slightly overlapping with the first spot, in which case the intensity of the voltammetric peak decreased, yielding only a shoulder on the feature attributed to Li UPD (panel B of Figure 7). As before, the solid and dotted lines in this figure represent
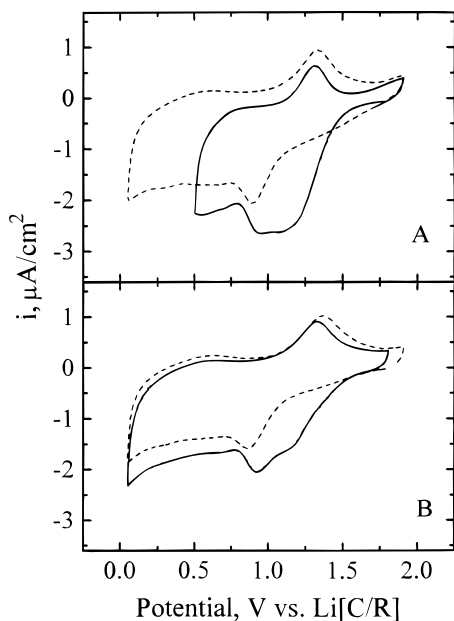
Figure 7. First (solid line) and second (dash line) voltammetric cycles of a Ni(110)−*c*(2× 2)-S in LiClO₄−PEO at 333 K (panel A). Scan rate was 5 mV/s. The results in panel B were obtained under the same conditions on another slightly overlapping spot on the same specimen (see text for details).

the first and second cycles. On the basis of a comparison between the first voltammograms in Figures 3 and 7 (solid lines), it is possible that the first scan obtained for a CO-saturated Ni(110) may also contain contributions due to residual sulfur on the surface.

In summary, the results of this investigation have shown that both carbon monoxide and sulfur adsorbed on Ni(111) and Ni(110), and presumably other nickel surfaces as well, give rise to pronounced changes in the first linear voltammetric scan in the negative direction in PEO(LiClO₄) at temperatures of about 333 K. In the case of Ni(111), rather sharp peaks were observed for *c*(4 × 2)CO and sulfur overlayers surfaces centered at 0.5 and 1.25 V, respectively. In contrast, the voltammetric features observed for Ni(110) exposed to 30 L of CO and for Ni(110)−*c*(2 × 2)S were rather broad and not as well defined. These

processes are believed to be due to interactions between Li UPD and CO in one case and S in the other, which react chemically to yield among other products Li₂O and Li₂S, respectively.

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