

Alkali insertion within NiO/Ni electrode in contact with molten $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ at 650 °C

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Abstract

Lithium, sodium and potassium species have been analysed by different spectroscopic techniques in the NiO layer recovering nickel cathode used in the state-of-the-art molten carbonate fuel cell. The nickel electrode was previously oxidized in lithium-containing carbonate electrolytes, $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ at 650 °C. Similarly to the well-known case of lithium, it has been shown that the presence of sodium and potassium cations could be associated to their insertion in the NiO lattice.

Keywords: Molten carbonate fuel cells; Lithium insertion; Sodium insertion; Potassium insertion; Lithium potassium carbonate; Lithium sodium potassium carbonate

1. Introduction

Lithium-doped nickel oxide offers various applications in promising fields such as lithium batteries with high energy density [1,2], molten carbonate fuel cells (MCFCs) [3–7] and catalytic activation of methane [8–10]. In effect, the insertion of lithium ions in the lattice of this oxide greatly affects its chemical and physical properties [11–13]. Furthermore, chemical and electrochemical intercalation/deintercalation of this ion in lithium nickel oxides have been described [14–17].

In general, when nickel is oxidized at high temperature a layer of non-stoichiometric NiO containing nickel vacancies is formed which causes the conduction in this oxide to be p-type [18]. These lattice defects play an important role in corrosion, catalysis and chemisorption. It has been shown that incorporation of alkali cations in NiO is realized preferentially according to [111] direction, yielding compounds of MNiO_2 type ($\text{M}=\text{Li}, \text{Na}$) with a layered structure [19,20]. In these compounds, alternate layers of alkali and nickel cations occupy the octahedral sites of a cubic-close packing of oxide ions, making up a rhombohedral structure. MNiO_2 and M_2NiO_2 compounds have been synthesized in different experimental conditions, some of which are summarized in Table 1. Although most of the alkali compounds investigated are lithium-promoted, as is the case in MCFC application, we have focussed our attention on sodium and

potassium-doped compounds in view of the selection of new carbonate electrolyte composition for MCFCs.

The aim of the present paper is to give experimental evidence of the incorporation of alkali ions in the NiO/Ni cathode used in MCFCs. On the one hand, very few studies have been dedicated to the delicate analysis of lithium in the NiO/Ni layer in contact with a lithiated carbonate melt¹. On the other hand, as far as we know, sodium and potassium have never been detected in the MCFC cathode. Two lithium-containing carbonate electrolytes were investigated at 650 °C: $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$. Open-circuit potential (OCP) of the electrochemical cell was measured for each melt, in order to analyse time evolution of the cathode. Lithium compounds were detected by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Sodium or potassium ions were analysed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) combined with energy dispersive analysis of X-ray (EDAX).

2. Experimental

Lithium, sodium and potassium carbonates mixed in a ratio of 43.5–31.5–25.0 mol% for $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ eutec-

¹ $\text{Li}_2\text{Ni}_{1-x}\text{O}$ porous cathodes used in MCFC can either be fabricated before incorporation into the cell, or formed in situ in the carbonate eutectic at operating temperature [5].

Table 1
Synthesis conditions of MNiO_2 compounds ($\text{M} = \text{Li}, \text{Na}$ or K)

Reactants	Temperature (°C)	Atmosphere	Time (h)	Products
$\text{NiO} + \text{Li}_2\text{CO}_3$	800	air		$\text{Li}_x\text{Ni}_{(1-2x)}^{2+}\text{Ni}_x^{3+}\text{O}$ [11]
$\text{Ni} + \text{Li}_2\text{CO}_3$	650	air	5	$\text{Li}_x\text{Ni}_{(1-x)}\text{O}$ [5]
$\text{Ni} + \text{Li}_2\text{CO}_3$	700	air	10	$\text{Li}_x\text{Ni}_{(1-x)}\text{O}$ [21]
$\text{NiO} + \text{Na}_2\text{O}$	500–800	O_2		NaNiO_2 [22]
$\text{NiO} + \text{Na}_2\text{O}$	600			Na_2NiO_2 [23]
$\text{NiO} + \text{Na}_2\text{O}$	650	O_2 (1 bar)		$\text{Na}_{0.91}\text{NiO}_2$ [24]
$\text{NiO} + \text{Na}_2\text{O}$	650	air	160	NaNiO_2 [25]
$\text{NiO} + \text{Na}_2\text{O}$ (1:1.1)	600		24	Na_2NiO_2 [26] (needles)
$\text{NiO} + \text{Na}_2\text{O}$ (1:1.1)	680		3–4 days	Na_2NiO_2 [26] (single crystal)
$\text{NiO}_{1.05} + \text{KO}_{0.56}$	500	Ar	7	K_2NiO_2 [27]
$\text{NiO} + \text{K}_2\text{O}$ (1:1)	400	O_2	i	K_2NiO_3 [28]

tic and 62.0–38.0 mol% for Li_2CO_3 – K_2CO_3 eutectic, were Merck reagents of analytical purity (>98%). The electrochemical cell and the reference electrode were described in Ref. [6]. The working electrode was a nickel foil (Johnson Matthey, analytical purity 99.99%) of 10 mm × 10 mm × 1 mm hanging from a nickel wire.

Different spectroscopic techniques were used to analyse the nickel foil:

(i) FT-IR with a Bruker IFS48 spectrometer (samples were 5 mm disks formed after pressing the product obtained by scratching the nickel foil mixed with CsBr);

(ii) XRD with a CGR type Théta 60 diffractometer using a $\text{Co K}\alpha$ radiation ($\lambda = 1.789 \text{ \AA}$);

(iii) SEM associated to energy dispersive analysis of X-ray EDAX (JEOL T330A), and

(iv) XPS with a VGEscalab MarkII spectrometer using the $\text{Al K}\alpha$ X-ray source. $\text{C}(1s)$ peak at 285 eV was used as an internal reference.

2.1. Experimental procedure

A nickel foil was introduced in molten carbonate binary or ternary eutectic at 650 °C under a $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm) gaseous environment (medium often used in the MCFC literature but its acidity is weaker than that used in MCFC conditions: $p\text{CO}_2$ (0.3 atm)). The OCP was registered until no evolution was observed. Then, the sample was removed from the molten mixture, air-cooled and rinsed as follows: (i) introduced in de-ionized water at 80 °C until solid carbonate deposits disappeared; (ii) rinsed and kept in de-ionized water for 5 h (changing the water two or three times), and (iii) dried on a filter-paper.

3. Results and discussion

A nickel electrode dipped in a molten carbonate eutectic, Li_2CO_3 – K_2CO_3 [29] or Li_2CO_3 – Na_2CO_3 – K_2CO_3 [30],

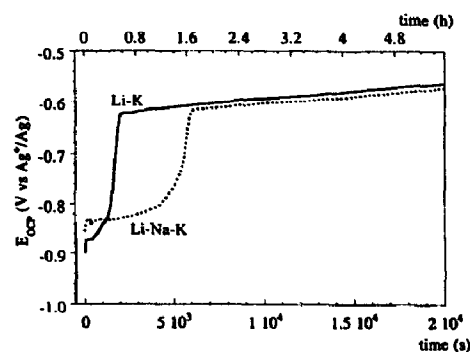


Fig. 1. Open-circuit potential of a nickel foil in Li_2CO_3 – K_2CO_3 and Li_2CO_3 – Na_2CO_3 – K_2CO_3 at 650 °C under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm).

under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm) at 650 °C, is oxidized and recovered with an NiO layer. Fig. 1 shows the evolution of the OCP in both melts. A stable value was reached after 34 min in Li_2CO_3 – K_2CO_3 and 100 min in Li_2CO_3 – Na_2CO_3 – K_2CO_3 . This difference is probably due to the higher lithium content in the binary eutectic. According to Nishina et al. [29], insertion of lithium cations in the NiO lattice is correlated with a significant potential shift, observed when following the OCP evolution of a nickel electrode. Therefore, after reaching a stable value of this potential, insertion process should be totally achieved. Other compounds showing a similar evolution of the OCP with respect to the insertion rate of alkali ions have been described in Refs. [31,32].

3.1. Analysis of lithium

The room-temperature infrared spectra of the nickel foil treated in Li_2CO_3 – K_2CO_3 , represented in Fig. 2, allowed the presence of lithium and nickel compounds to be detected. By analogy with the studies of Hewston and Chamberland [33] and Tarte and Preudhomme [34], LiO_6 vibrations can be observed in the low energy region at 260.7 cm^{-1} , while

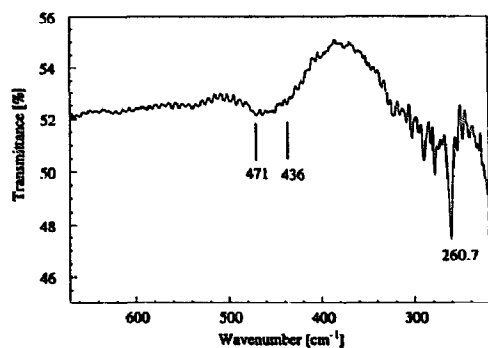


Fig. 2. Infrared spectra of a nickel foil after treatment in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ at $650\text{ }^\circ\text{C}$ under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm).

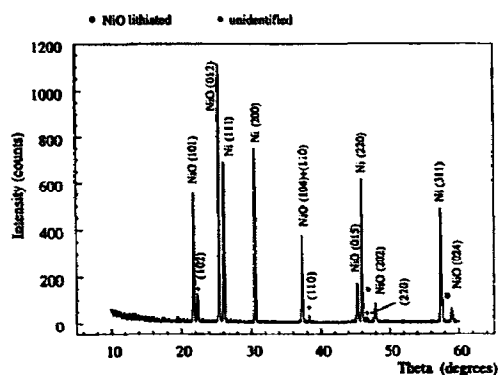


Fig. 3. X-ray diffraction pattern of a nickel foil after treatment in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ at $650\text{ }^\circ\text{C}$ under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm).

absorptions at higher energies between 436 and 471 cm^{-1} can be associated with the octahedral NiO_6 . Similar results were obtained with the ternary eutectic.

XRDs of the nickel foil treated in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ or $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ also confirm the presence of lithiated NiO: $\text{Li}_x\text{Ni}_{1-x}\text{O}$. Ni and NiO lines were identified in the XRD pattern shown in Fig. 3. Among the lines corresponding to the lithiated compound, only (102), (110) and (220) were observed. Line (104) which should be the more intense, according to data in Refs. [14,35] is masked by line Ni(111). Line (003) was not observed, in agreement with the observations of Morales et al. [14]. These authors observed that the intensity of this line depends on the distribution of lithium and nickel ions in the oxide lattice and when the Li:Ni ratio is low, line (003) does not appear. Incorporation of lithium in the NiO lattice was also described in Refs. [36,37]. Furthermore, in studies concerning the behaviour of lithium nickelate compounds at temperatures lower than $650\text{ }^\circ\text{C}$, lithium insertion has been described as an intercalation process [14,17]. Nevertheless, reversibility of this reaction² has not been analysed in MFCFC conditions at $650\text{ }^\circ\text{C}$

² Insertion and intercalation processes have been fully described in the literature [38].

and we cannot conclude whether or not it is an intercalation phenomenon.

3.2. Analysis of sodium and potassium

X-ray photoelectron spectra (XPS) of the nickel foil in the ternary eutectic before and after sputtering is given in Fig. 4. Two energy peaks at 293 and 500 eV, corresponding to $K2p_{3/2}$ and the Auger peak of sodium ($\text{Na } KL_{23}L_{23}$) confirm the presence of both alkali species in a superficial layer of about 20 \AA . By comparing areas in the two spectra, shown in Fig. 4(a) and (b), a significant amount of sodium remains in the NiO/Ni layer after sputtering. A smaller amount of potassium remains after sputtering. It must be noted that the peak corresponding to C(1s) dramatically decreased after sputtering. This indicates that the presence of sodium after sputtering is not due to sodium carbonate. It is more difficult to conclude in the case of potassium. In fact, the interaction between sodium and potassium with NiO has been studied by other authors at temperatures close to $650\text{ }^\circ\text{C}$ used in MFCFCs [20,39,40]. They concluded that potassium penetrates within the NiO clusters [40] and that sodium nickelate is formed [20].

It is worth noting that hygroscopic sodium or potassium nickelates can be partially removed in the aqueous phase by rinsing the samples [22,41–43]³. This means that the amounts of sodium or potassium detected could probably be inferior to those initially present in the NiO layer before rinsing.

Sodium and potassium insertion was confirmed by SEM spectroscopy when layers of about $0.5\text{ }\mu\text{m}$ being investigated. The thickness of the layers corresponds approximately to that of the NiO layer ($0.3\text{ }\mu\text{m}$) measured by Ogura et al. [44] in Li–K eutectic at $650\text{ }^\circ\text{C}$. Fig. 5(a) shows a SEM picture realized with a nickel sample after treatment in the ternary eutectic. Dark and clear spots can be observed in this sample. According to the studies on lithiated NiO by Decker et al. [45], the clear substrate is lithium-poor and the dark spots correspond to a phase with strong intercalation of lithium ions. This tends to confirm lithium insertion and, probably, the insertion of sodium and potassium. Fig. 5(b), representing an X-ray probe microanalysis (EDAX) of the same sample, allows a significant amount of both sodium and potassium species to be observed. The fact that these species are detected in a layer of about $0.5\text{ }\mu\text{m}$ discards the hypothesis of an adsorption and is more in agreement with their insertion in the NiO lattice and formation of sodium and potassium nickelates.

XPS of a nickel sample previously dipped in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic (Fig. 6) clearly shows that the same amount of potassium was present in the NiO layer before and after sputtering. In this case small amounts of carbon were still

³ Hydrolysis of NaNiO_2 and KNiO_2 yields NiOOH ($\text{MNiO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NiOOH} + \text{MOH}$) [22,41,43]. Hydrolysis of K_2NiO_2 yields KOH and NiO [28].

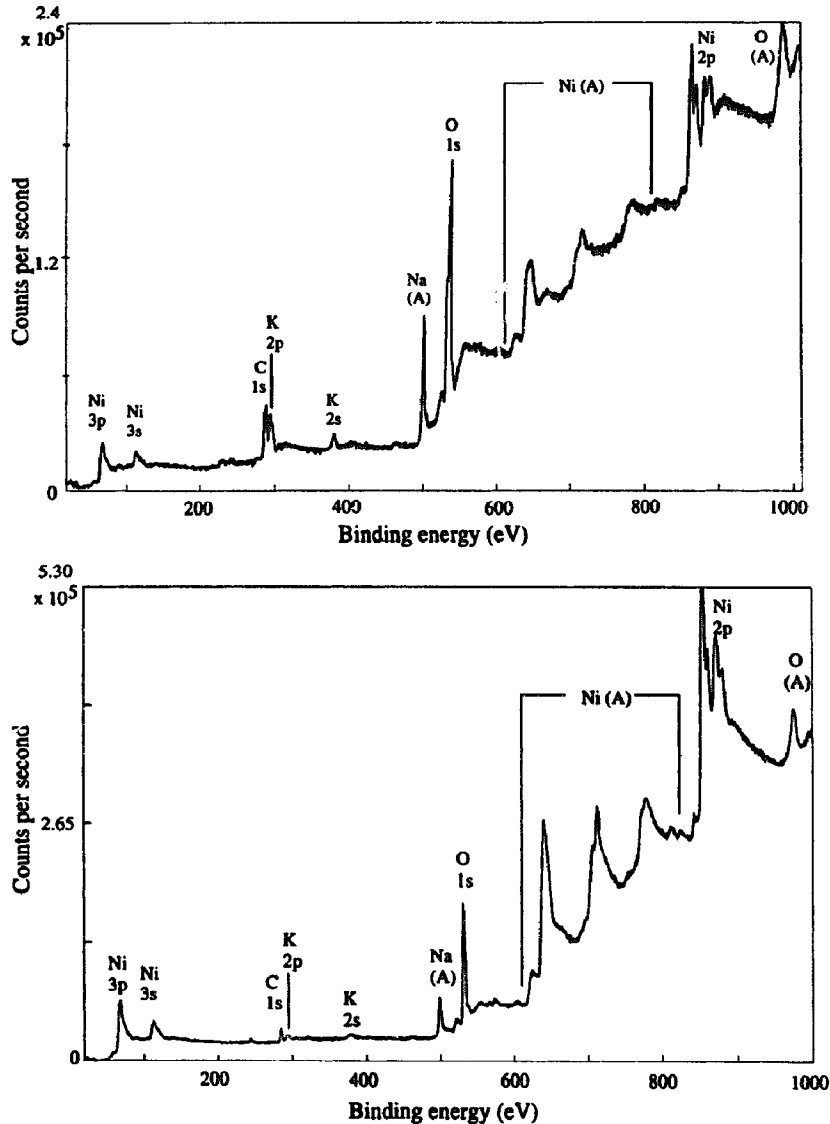


Fig. 4. General X-ray photoelectron spectra of a nickel foil after treatment in $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ at 650°C under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm): (a) before sputtering, and (b) after argon sputtering ($p\text{Ar}: 2 \times 10^{-7}$ mbar, acceleration tension: 4 kV, current: $40 \mu\text{A}$, and duration: 2 min).

present after sputtering but in a proportion much lower than that of $\text{K}2\text{p}$ peak.

According to our experimental results and data in the open literature, it can be assessed that lithium ions are incorporated in the NiO lattice under a lithium nickelate form. Insertion of sodium and to a certain extent of potassium seems also to take place in the NiO lattice. It is likely that the insertion of alkali ions is facilitated in a molten salt in comparison with solid state reactions commonly studied. Nevertheless, still many questions have yet to be answered. What really happens in the NiO lattice, is it the formation of a single mixed compound containing alkali cations, or different crystalline structures? In a recent paper, the electrochemical intercalation of alkali ions separately ($\text{Li}^+ > \text{Na}^+ > \text{K}^+$) in an amorphous

WO_3 film has been described [46], which allows to believe that alkali insertion in NiO/Ni, and in particular of sodium and potassium, can be considered as realistic. It is worth mentioning that a new layered alkali-transition metal oxide was prepared and characterized: $\text{Li}_{0.43}\text{Na}_{0.36}\text{CoO}_{1.96}$ [47]. In this compound, Li^+ are sited within an octahedral framework whereas Na^+ are within a trigonal prismatic environment (between CoO_6 layers). We could imagine the same kind of structure with NiO, including lithium and sodium (with may be potassium). Of course, a substantial distortion of the well-known structure of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ may occur. Further spectroscopic and structural studies are necessary to explain the insertion mechanism and the transformation of the NiO lattice.

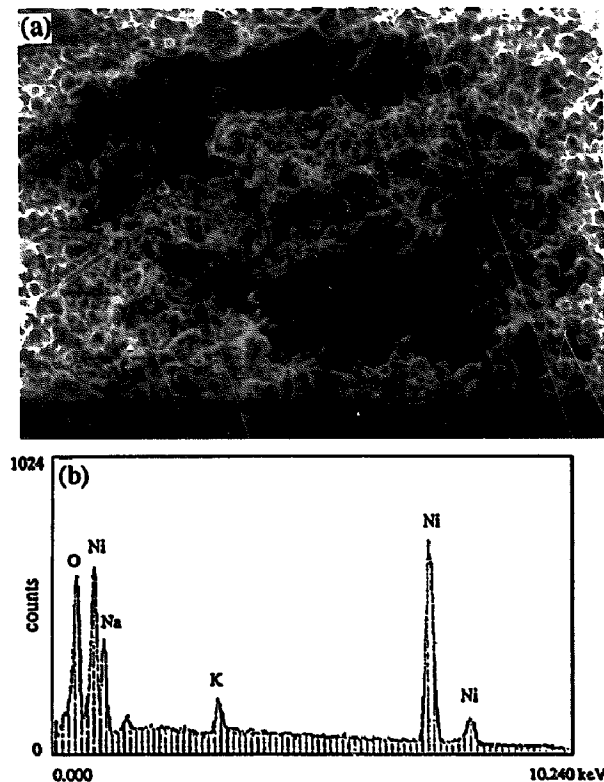


Fig. 5. Nickel foil after treatment in $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ at 650°C under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm): (a) SEM micrograph, and (b) energy dispersive analysis of X-ray (EDAX).

4. Conclusions

Lithiated NiO has been detected within the NiO layer recovering a nickel electrode in contact with the two mentioned carbonate eutectics. The presence of sodium and potassium ions, never mentioned before in these conditions, has also been observed. It can be concluded from our results that insertion of lithium, sodium and potassium takes place in the NiO lattice. In the case of the ternary eutectic $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$, mixed compounds are probably formed with a higher proportion of lithium with respect to sodium. Potassium insertion appears to be less important. In the case of $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$ eutectic, mixed nickelate compounds could be formed in the NiO lattice, with probably a high content of lithium and traces of potassium.

This work constitutes a first step for a better understanding of sodium and potassium insertion within MCFC cathode and, consequently, for the optimization of the molten carbonate eutectic composition and the electrode material.

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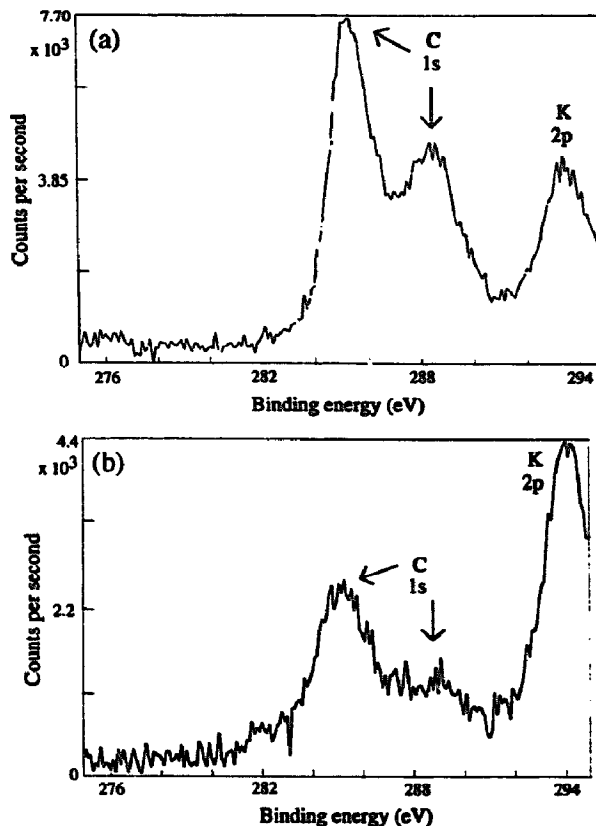


Fig. 6. X-ray photoelectron spectra of a nickel foil after treatment in $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3$ at 650°C under $p\text{CO}_2$ (0.1 atm) + $p\text{O}_2$ (0.9 atm): (a) before sputtering, and (b) after argon sputtering ($p\text{Ar}$: 2×10^{-7} mbar, acceleration tension: 4 kV, current: 40 μA , and duration: 2 min).

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