

## ORIGINAL PAPER

M. Mohan Rao · M. Jayalakshmi · O. Schäf · U. Guth  
H. Wulff · F. Scholz

## Electrochemical behaviour of solid lithium nickelate (LiNiO<sub>2</sub>) in an aqueous electrolyte system

Received: 18 February 1999 / Accepted: 5 May 1999

**Abstract** Lithium nickelate was synthesized by self-propagating high-temperature combustion. The electrochemical behaviour of the product was studied by cyclic voltammetry of microparticles immobilized on the surface of graphite electrodes. Whereas numerous previous studies have dealt with non-aqueous electrolyte solutions, here the behaviour of lithium nickelate in contact with aqueous electrolyte solutions was investigated. It could be shown that protons are intercalating upon reduction of the Ni(III) to Ni(II) and deintercalating upon oxidation. This insertion electrochemistry is chemically reversible. Within 1600 oxidation-reduction cycles, the response diminished only by about 10%. Scanning electron microscopy reveals a considerable recrystallization during the electrochemical cycles. Energy dispersive X-ray detection proved that no metal cations are intercalating. The electrochemical system is accessible only in very alkaline solutions as it shifts to more positive values with decreasing pH.

**Key words** Lithium nickelate · Solid state electrochemistry · Proton intercalation · Voltammetry · Immobilized microparticles

### Introduction

Oxide materials such as LiNiO<sub>2</sub> and LiCoO<sub>2</sub> and similar compounds are promising candidates as electrode ma-

terials for rechargeable lithium batteries [1, 2] and more specifically for the rocking-chair type with carbon as the negative electrode. In view of these applications, the structure and electrochemistry of lithium nickelate with non-aqueous electrolytes has been well studied. It has been reported that lithium nickelate crystallizes in the rhombohedral lattice mode with trigonal symmetry (space group: *R3m*). The lithium and nickel ions occupy the octahedral sites of the face-centred cubic oxygen packing. Depending upon the value of *x* in Li<sub>*x*</sub>Ni<sub>1-*x*</sub>O<sub>2</sub>, various authors report distortions in the structure of the compound [3–5]. If *x* < 0.56, the structure of lithium nickelate is that of the disordered rock salt type, whereas for *x* > 0.6, partial cation ordering occurs, culminating in the formation of the layered LiNiO<sub>2</sub> (*α*-NaFeO<sub>2</sub>) structure at *x* = 1. The layered compound is very important from the battery point of view, since it is the only phase known to intercalate lithium ions reversibly at voltages larger than 3.5 V vs. Li. Using electrochemical and *in situ* X-ray techniques, it was proved that LiNiO<sub>2</sub> can be electrochemically converted into Li<sub>2</sub>NiO<sub>2</sub> by insertion of lithium ions and vice versa, though substantial hysteresis in the cell voltage was observed during this phase transition [6]. Several attempts were made to prepare the stoichiometric compound but the results were not successful. Even a small amount of structural disorder due to the displacement of nickel ions or lithium ions in the structure of LiNiO<sub>2</sub> leads to changes in the electrochemical properties of the sample [7, 8]. Electrochemical studies on the variation of cell voltage vs. composition of LiNiO<sub>2</sub> revealed that the increase in the content of nickel ions in the sample decreases the discharge capacity of Li/Li<sub>*x*</sub>Ni<sub>1-*x*</sub>O<sub>2</sub> cells in propylene carbonate [1]. The extra nickel ions present in the lithium sites reduce the interslab space and this limits the reintercalation of lithium ions during discharge, thereby affecting the cell performance. Also the electrostatic repulsion between the lithium ions and the extra nickel ions may play a negative role in the entry of lithium ions. These materials as well as the sodium compounds are also used as reference systems in solid

M. Mohan Rao · M. Jayalakshmi · O. Schäf · U. Guth<sup>1</sup>  
H. Wulff · F. Scholz (✉)  
Institut für Chemie und Biochemie,  
Ernst-Moritz-Arndt-Universität Greifswald,  
Soldmannstraße 23, D-17487 Greifswald, Germany  
e-mail: fscholz@rz.uni-greifswald.de,  
Tel.: +49-3834-864450, Fax: +49-3834-864451

*Present address:*

<sup>1</sup> Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V.,  
Meinsberg, Germany

state  $\text{CO}_2$  and  $\text{SO}_2$  sensors using  $\beta''$ -alumina as a solid electrolyte. Very fine powders are necessary to form reference electrodes that are electrochemically active [9, 10].

Conventionally, these oxide materials are prepared by a solid state method [1, 6, 8], which is a tedious and time consuming process, involving prolonged heating with intermittent cooling and grinding of the powders. A key focal point in materials chemistry is the development of new routes for the preparation of a variety of inorganic compounds with the desired structure, composition and properties. In the present work,  $\text{LiNiO}_2$  is prepared by self-propagating high-temperature combustion (SPHTC). This is a novel technique that has been used successfully for the preparation of ceramic and phosphor materials [11–16]. The main advantage of this method, compared to the solid state sintering method, is that the experiment is completed within 10 min. The basic principle of the method is the decomposition of an oxidizer, e.g., a metal nitrate, in the presence of a fuel. The fuel becomes ignited by the oxidizer to yield oxide materials derived from the metal salts.

$\text{LiNiO}_2$  prepared by SPHTC is subjected to electrochemical studies in aqueous electrolytes by mechanically immobilizing the solid sample on the surface of a paraffin impregnated graphite electrode (PIGE) [17–20]. It is worth mentioning that this material is so far studied only for its electrochemical behaviour in non-aqueous electrolytes and to our knowledge there have been no previous reports available on the electrochemistry of  $\text{LiNiO}_2$  in aqueous electrolytes. We focused our attention to study the electrochemical behaviour of this compound in aqueous electrolytes in order to examine its insertion characteristics so that its viability as a battery active material could be extended to aqueous systems. In this paper we report the cyclic voltammetric behaviour of  $\text{LiNiO}_2$  in aqueous alkali electrolytes, which helps to understand the intercalation and deintercalation of cations during the redox process. With the help of scanning electron microscopy (in conjunction with an energy-dispersive X-ray spectrometer), the electrochemically treated electrodes were analysed for the presence of intercalated cations. The composition of the lithium nickelate powder prepared was characterized by X-ray diffraction.

## Experimental

### Preparation of $\text{LiNiO}_2$ by SPHTC

In SPHTC, attention should be given to calculating the stoichiometric composition of the oxidizing and reducing species in order to obtain phase-pure final products and also to avoid the evolution of unwanted gases like  $\text{NO}_2$  during the combustion process. Some details regarding the experimental procedure for the preparation of  $\text{LiNiO}_2$  by SPHTC are given below.

The stoichiometric compositions of the redox mixtures for the combustion reaction are calculated, using the total oxidizing ( $O$ ) and reducing ( $R$ ) valencies of the individual components, which

serve as the numerical coefficients for the stoichiometric balance, so that the equivalent ratio,  $R_e$  is unity (i.e.  $O:R = 1$ ) and the energy released by combustion is a maximum [21]. Accordingly, the stoichiometric composition of the reaction mixture is calculated for the synthesis of  $\text{LiNiO}_2$  as:  $\text{LiNO}_3 + \text{Ni}(\text{NO}_3)_2 + 2.5 \text{NH}_2\text{-CO-NH}_2$ .

As per the above equation the stoichiometric amounts of the reactants, viz.  $\text{LiNO}_3$ ,  $\text{Ni}(\text{NO}_3)_2$  and urea, were dissolved in a minimum amount of distilled water in a beaker. The beaker with the solution was subjected to heating in a muffle furnace at  $500^\circ\text{C}$ . After a few minutes the solution boiled, solidified and ignited with a flame temperature of  $1100^\circ\text{C}$  to yield a grey-black fine powder.

### Equipment and measurements

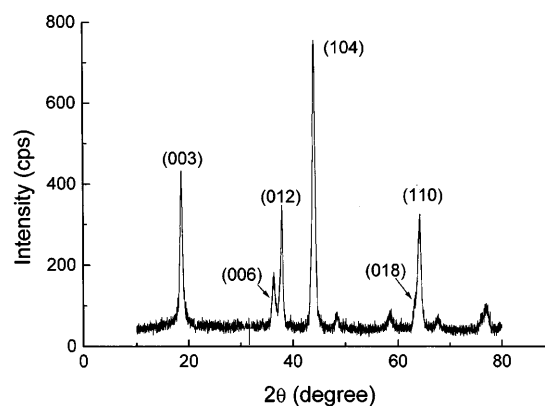
For electrochemical measurements the following instrumentation was used: an Autolab (ECO-Chemie, Utrecht, Netherlands), an electrode stand VA 663 (Metrohm, Herisau, Switzerland) and a 386 personal computer. The reference electrode (Metrohm, Switzerland) was an  $\text{Ag}/\text{AgCl}$  electrode with 3 M  $\text{KCl}$  ( $E = 0.208 \text{ V}$  vs. SHE). All measurements were performed in solutions which were thoroughly deaerated with high-purity nitrogen for at least 10 min. The voltammograms were recorded at  $22 \pm 1^\circ\text{C}$ . X-ray diffraction (XRD) measurements were performed with a HZG 4 (Seifert-SPM, Germany) and the scanning electron microscope was a Leo 440 (Germany) equipped with an Econ 4 detector (EDAX, USA).

All the chemicals used were of analytical grade and all solutions were prepared with double distilled water.

## Results and discussion

### XRD studies

The XRD pattern of the  $\text{LiNiO}_2$  sample prepared by SPHTC is shown in Fig. 1. The X-ray pattern is comparable with the standard JCPDS data [22]. Although the  $2\theta$  values are comparable with the standard pattern of  $\text{LiNiO}_2$ , there are considerable differences in the intensity of lines (003) and (104). This may be due to the formation of a lithium-deficient phase  $\text{Li}_{1-x}\text{NiO}_2$ . The value of  $x$  in the sample can be deduced by comparing the X-ray data of  $\text{LiNiO}_2$  reported in earlier studies. Our XRD pattern and data coincide with the work of

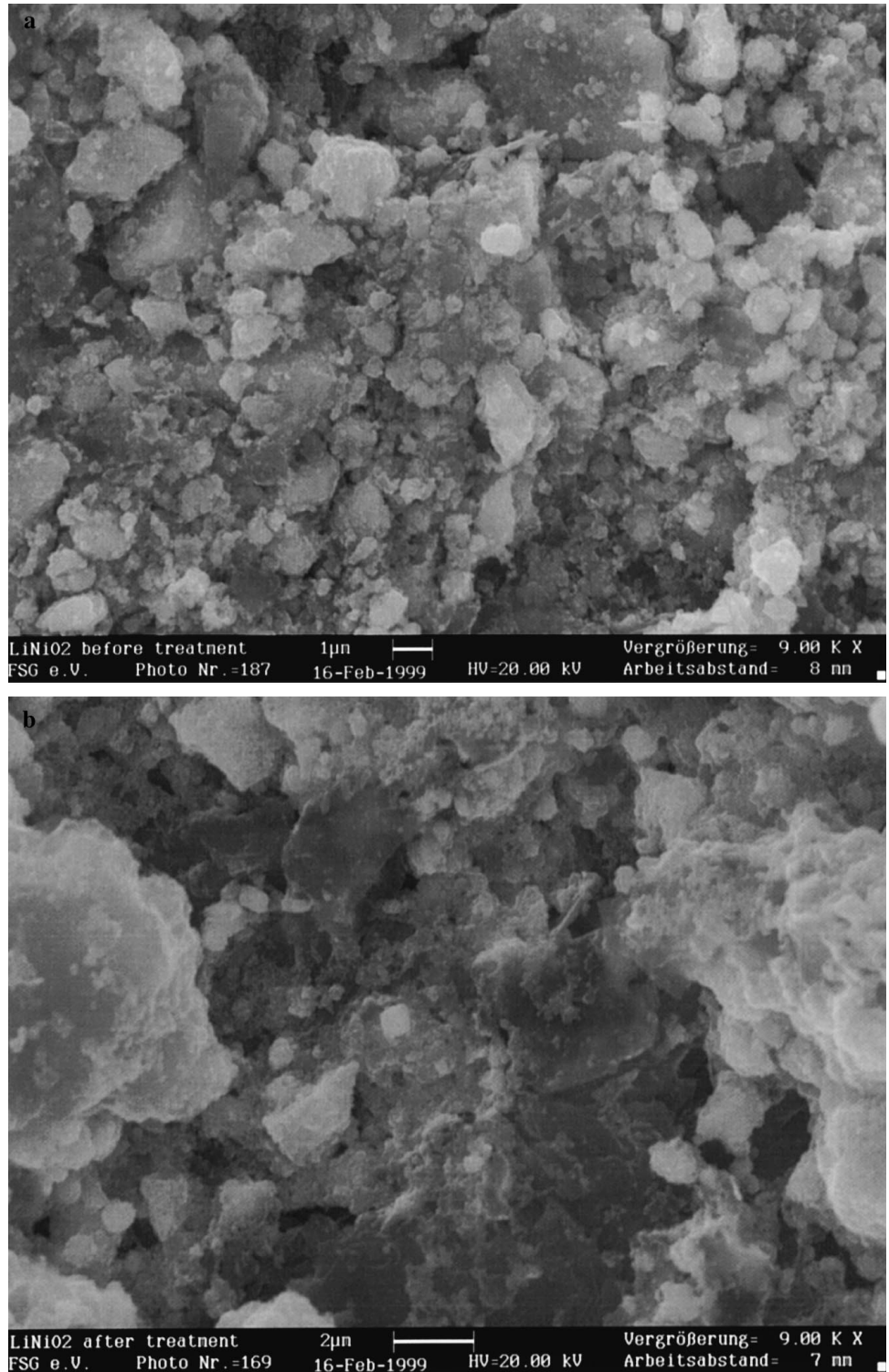


**Fig. 1** X-ray diffraction (XRD) pattern of  $\text{LiNiO}_2$  prepared by self-propagating high-temperature combustion (SPHTC)

Rougier et al. [1], who deliberately prepared a lithium-deficient phase of  $\text{LiNiO}_2$ . They reported an  $x$  value of 0.41 for a thermally treated sample at  $950^\circ\text{C}$ , which may hold good for our sample since the SPHTC involves a high temperature ( $1100^\circ\text{C}$ ). From this we infer that the composition of samples prepared by our method is  $\text{Li}_{0.6}\text{NiO}_2$ . As reported by Rahner et al. [23],  $\text{Li}_{1-x}\text{NiO}_2$

with  $0 \leq x \leq 0.5$  is a suitable cathode material for rechargeable lithium cells using a carbon anode. The broadening of the XRD lines (Fig. 1) of the sample is due to the smaller size of the crystallites. It is known, in general, that SPHTC produces samples of fine particle size. Scanning electron microscopy of  $\text{LiNiO}_2$  shows the particle morphology as in Fig. 2.

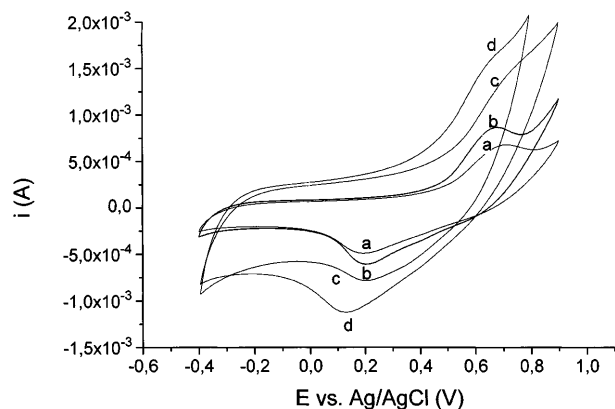
**Fig. 2** Scanning electron microscopy (SEM) image of  $\text{LiNiO}_2$  **a** before electrochemical treatment and **b** after electrochemical treatment with a final reduction at 0.1 V vs. Ag/AgCl



## Electrochemical studies

As mentioned in the introductory part of this paper, the structure and electrochemistry of lithium nickelate is well studied in non-aqueous electrolytes with reference to its application as a positive electrode in the recently developed rocking-chair rechargeable batteries. The structure of lithium nickelate determines the insertion phenomena, which in turn decide the applicability of the compounds. In the case of iron(III) hexacyanoferrate(II) or Prussian blue (PB), the zeolitic channels of PB enable a reversible intercalation of lithium ions from non-aqueous electrolytes [24] but not from aqueous electrolytes. This is the result of the very strong hydration of lithium ions and the large size of the hydrated ions. An appreciable difference between  $\text{LiNiO}_2$  and PB is that the layered interslab spacing in the structure of  $\text{LiNiO}_2$  is variable with respect to the mode of preparation, whereas the zeolitic channel of PB remains unperturbed and insensitive to the method of preparation ([25] and refs. therein). This study was aimed at elucidating whether  $\text{LiNiO}_2$  can reversibly intercalate cations from aqueous electrolytes. To study this problem, cyclic voltammetry of microparticles of the compound immobilized on graphite electrodes was applied [26]. Aqueous alkali electrolytes were used in these studies. Our attempts to study this compound in neutral solutions were not successful because of the pH shift of the voltammetric system with decreasing pH.

Lithium nickelate powder was mechanically immobilized on the surface of a PIGE and the electrode was cycled in LiOH, NaOH and KOH electrolyte solutions of varying concentrations ranging from 0.02 to 0.5 M. Figure 3 shows the cyclic voltammograms obtained for lithium nickelate in LiOH electrolyte solutions. The appearance of a single set of strong and stable redox peaks indicates that intercalation and deintercalation of cations take place during the faradaic redox reaction. At a low concentration of the electrolyte (0.02 M), the an-



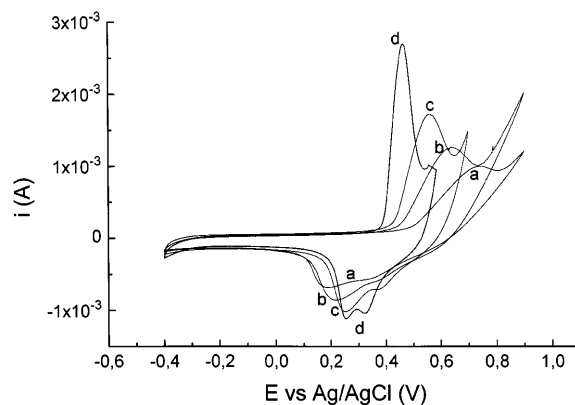
**Fig. 3** Cyclic voltammograms of mechanically immobilized  $\text{LiNiO}_2$  on the surface of a paraffin impregnated graphite electrode (PIGE) in different concentrations of LiOH electrolyte solutions: a 0.02 M, b 0.04 M, c 0.05 M, d 0.1 M. Scan rate =  $50 \text{ mV s}^{-1}$

odic peak occurred at 0.76 V and the cathodic peak at 0.2 V. With increasing concentration of the electrolyte, the anodic peak is shifted towards negative potentials while the cathodic peak is shifted towards positive potentials. At higher concentrations of the electrolytes (0.05 and 0.1 M), the anodic peak tends to disappear.

It is interesting to speculate about the origin of the redox peaks in LiOH electrolyte solutions. In propylene carbonate + 1 M  $\text{LiClO}_4$  electrolyte solutions [23],  $\text{LiNiO}_2$  gives a single set of redox peaks which are due to the reversible intercalation of lithium ions. However, in aqueous electrolytes the identity of the cation which is reversibly intercalating is not known. The anodic peak probably appeared owing to the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  in  $\text{LiNiO}_2$  accompanied by the expulsion of a cation, and the cathodic peak may be due to the reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  accompanied by the intercalation of a cation. The reaction may be written as



Figure 4 shows the cyclic voltammograms of  $\text{LiNiO}_2$  in various NaOH electrolyte solutions. There is a pronounced difference in the behaviour of  $\text{LiNiO}_2$  in NaOH compared to that of LiOH electrolyte solutions. At higher concentrations, say at 0.1 and 0.5 M NaOH solutions, the anodic peak is sharp and well defined, indicating that the faradaic reaction involving the ion expulsion is much more facile than in case of LiOH solution. Apart from this fact, other characteristics of the cyclic voltammograms remain similar to LiOH. With an increase in the concentration of NaOH, the anodic peak shifts towards negative potentials. At the highest studied concentration of NaOH (0.5 M), the anodic peak appears as if it is a doublet. At 0.1 M NaOH, the anodic peak is preceded by a precursor peak which is less predominant at lower concentrations. As seen from the cyclic voltammograms, it becomes more pronounced with increasing concentration and appears as a doublet or split peak. Such peak splitting has been reported for



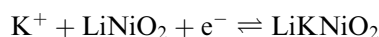
**Fig. 4** Cyclic voltammograms of mechanically immobilized  $\text{LiNiO}_2$  on the surface of a PIGE in different concentrations of NaOH electrolyte solutions: a 0.02 M, b 0.05 M, c 0.1 M, d 0.5 M. Scan rate =  $50 \text{ mV s}^{-1}$

PB films in NaCl solutions [27] and also for  $\text{LiMn}_2\text{O}_4$  in non-aqueous electrolyte [23]. The reason for such peak splitting is not clearly established. It was reported that such behaviour could arise from the transformation of one phase to another or be due to the difference in  $E_0$  values of two distinct chemical species formed.

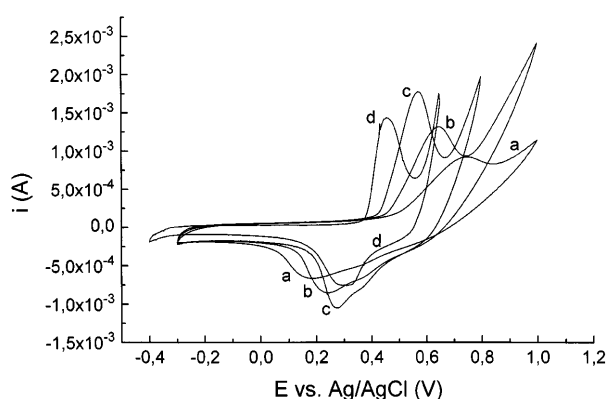
Figure 5 shows the cyclic voltammograms obtained for lithium nickelate in KOH electrolyte solutions with the concentration ranging from 0.02 to 0.5 M. The electrochemical behaviour of lithium nickelate in KOH is similar to that in NaOH except at the highest concentration studied (0.5 M), where there is reduction in peak current values of both the anodic and cathodic peaks. Again the precursor peak appearing before the anodic peak in NaOH is not clearly visible in KOH electrolyte solutions. The presence of such a peak seemed to be apparent in 0.02 M KOH, but with increasing concentration there is no predominant appearance of this peak.

In order to have a clear picture for comparison between the three alkali solutions, the cyclic voltammograms of lithium nickelate in 0.1 M LiOH, NaOH and KOH are shown in Fig. 6. At lower alkali concentration (0.02 M) the difference in peak potentials is minimal and they appear more or less at the same potentials, although the peak currents in the case of LiOH are smaller compared to those of the other two electrolyte solutions. However, at higher concentration (0.1 M) the cyclic voltammograms obtained for NaOH and KOH (Fig. 6) are similar in shape and potentials, but the result is different in LiOH.

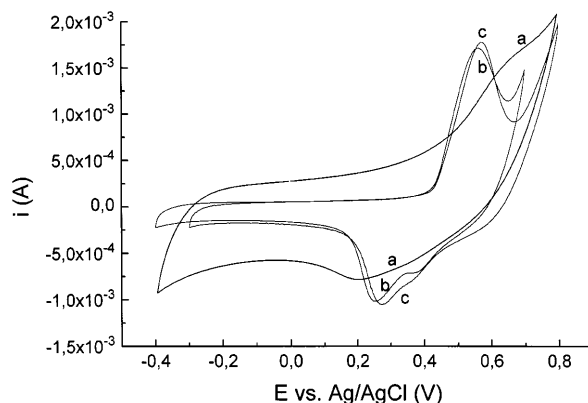
If we suppose that the intercalating cation is an alkali metal cation ( $\text{K}^+$  or  $\text{Na}^+$  or  $\text{Li}^+$ ) in these alkali electrolytes, then the equation representing the redox reaction may be written as



In accordance with this reaction one should, according to Nernst, observe the following dependence of the formal potential on the activity of the alkali cation:



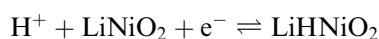
**Fig. 5** Cyclic voltammograms of mechanically immobilized  $\text{LiNiO}_2$  on the surface of a PIGE in different concentrations of KOH electrolyte solutions. *a* 0.02 M, *b* 0.05 M, *c* 0.1 M, *d* 0.5 M. Scan rate =  $50 \text{ mV s}^{-1}$



**Fig. 6** Comparison of cyclic voltammograms of mechanically immobilized  $\text{LiNiO}_2$  on the surface of a PIGE in 0.1 M electrolyte solutions: *a* LiOH, *b* NaOH, *c* KOH. Scan rate =  $50 \text{ mV s}^{-1}$

$$E_f = E^\circ + 0.059 a_{\text{K}^+}$$

i.e. the formal potential  $E_f = (E_a + E_c)/2$  of the redox reaction should be directly proportional to the concentration of potassium ions in KOH electrolyte solutions. Table 1 shows the formal potentials evaluated in various concentrations of the alkali electrolytes. As seen from the table, the formal potentials in all three cases decrease with increase in concentration of the alkali electrolyte solutions. This fact is more clear from the derived plots of  $E_f$  vs.  $\log[\text{K}^+]$  and  $E_f$  vs.  $\log[\text{Na}^+]$  in Fig. 7. These results indicate that the alkali metal cations do not intercalate in  $\text{LiNiO}_2$  from alkali electrolyte solutions. If we assume that the intercalating cation is a proton, then the equation for the redox reaction can be written as



Then, the Nernst equation follows as

$$E_f = E^\circ + 0.059 a_{\text{H}^+}$$

In this case, the formal potentials should be directly proportional to the concentration of protons in the alkali electrolyte solutions. The negative slope of the plots in Fig. 7 is in good agreement with the idea of proton participation in the redox reaction. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) results confirm this supposition, which will be discussed below.

Since the intercalating cation in all the three alkali electrolytes is the proton, the difference in cyclic vol-

**Table 1** Formal potentials of the  $\text{Ni}^{2+/3+}$  system of solid  $\text{LiNiO}_2$  at various concentrations of alkali hydroxide solutions

Conc. MeOH ( $\text{mol l}^{-1}$ )	$E_f$ (V) LiOH	$E_f$ (V) NaOH	$E_f$ (V) KOH
0.02	0.479	0.463	0.472
0.03	0.462	0.452	0.455
0.04	0.437	0.445	0.432
0.1	–	0.399	0.417
0.5	–	0.355	0.377

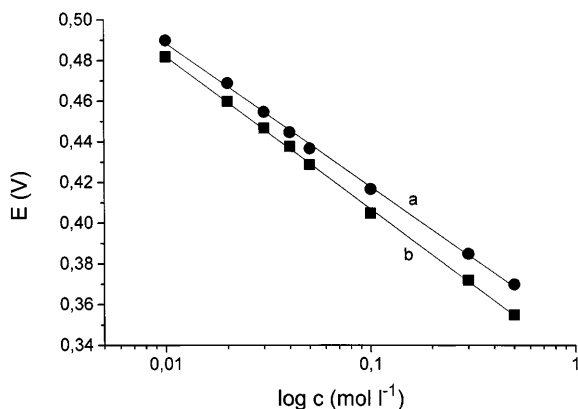


Fig. 7 Derived plots of *a*  $E_f$  vs.  $\log[K^+]$ , *b*  $E_f$  vs.  $\log[Na^+]$

tammetric behaviour obtained at higher concentrations (Fig. 6) still needs to be explained. The most probable explanation is to take into account the variation of activity coefficients in the different alkali hydroxide solutions. A study of the scan rate dependence of the peak currents reveals that the reaction is diffusion limited at scan rates above  $100 \text{ mV s}^{-1}$  ( $i_{p,c} \sim \sqrt{v}$ ) (Fig. 8a). At lower scan rates the peak currents are proportional to the scan rate (Fig. 8b), which is due to the very small particles allowing complete electrolysis during the time scale of the experiment.

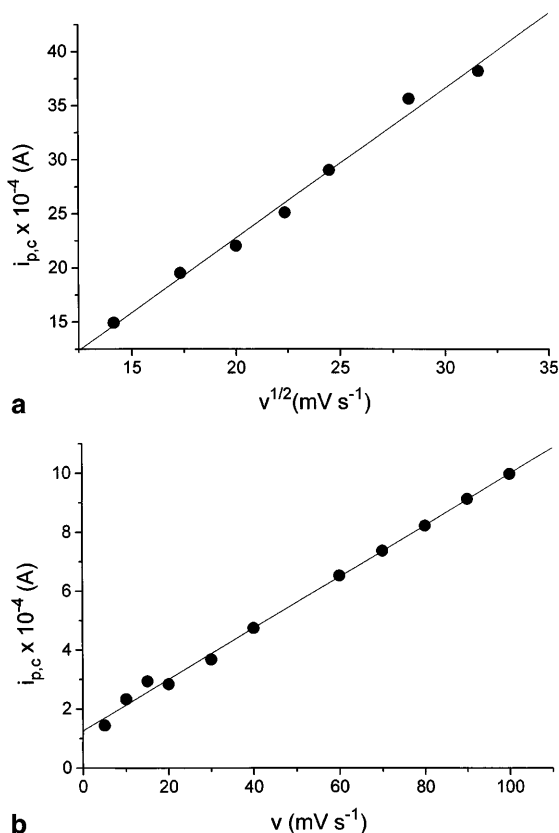


Fig. 8 Plots of *a*  $i_{p,c}$  vs.  $\sqrt{v}$  *b*  $i_{p,c}$  vs.  $v$  ( $v$ : scan rate)

In long-term experiments with continuous cycling ( $100 \text{ mV s}^{-1}$ ) of  $\text{LiNiO}_2$  in  $0.5 \text{ M KOH}$  it was observed that the voltammetric system decreased only by about 10% within 1600 cycles between  $-0.2 \text{ V}$  and  $+1.0 \text{ V}$  vs.  $\text{Ag/AgCl}$ . The reason for this decrease may be a small loss of microparticles adherent to the electrode surface as a result of the recrystallization which is obvious from Fig. 2. It is rather improbable that the  $\text{LiNiO}_2$  itself caused this loss of response. This feature needs a separate study if a battery application of the system is to be attempted.

#### SEM-EDX studies

The SEM-EDX spectrum obtained for  $\text{LiNiO}_2$  powder prior to electrochemical treatment shows only Ni signals. As expected, there is no intercalated cation in the sample. Also the EDX spectrum of a  $\text{LiNiO}_2$  sample which is electrochemically treated does not show any metal other than nickel. The sample was subjected to a cycle of intercalation/deintercalation processes through chronocoulometric experiments. Initially the electrode was oxidized at  $0.5 \text{ V}$  for 10 min (deintercalation) and then reduced at  $0.1 \text{ V}$  for 10 min (intercalation) in  $0.5 \text{ M KOH}$  electrolyte solution. The absence of a signal for  $K^+$  ions in the EDX spectrum reveals that these ions do not intercalate during the redox reaction. These results clearly augment our arguments and conclusions arrived through electrochemical studies.

#### Conclusions

This study shows for the first time that lithium-deficient lithium nickelate  $\text{Li}_{1-x}\text{NiO}_2$  undergoes a chemically reversible proton intercalation electrochemistry in aqueous alkali electrolytes. This is even in  $\text{LiOH}$  the preferable reaction pathway, most certainly because of the very strong hydration of lithium ions.

**Acknowledgements** M.J. acknowledges provision of a fellowship from Humboldt Stiftung. M.M.R. acknowledges funding by Deutsche Forschungsgemeinschaft. This work was additionally supported by Fonds der Chemischen Industrie.

#### References

- Rougier A, Gravereau P, Delmas C (1996) *J Electrochem Soc* 143: 1168
- Nakai I, Takahashi K, Shiraishi Y, Nakagome T (1997) *J Phys (Paris) IV France 7: C2-1243 Colloq (J Phys (Paris) III Suppl)*
- Goodenough JB, Wickham DC, Croft WJ (1958) *J Phys Chem Solids* 5: 107
- Goodenough JB, Wickham DC, Croft WJ (1958) *J Appl Phys* 29: 382
- Bronger VW, Bade H, Klemm W (1964) *Z Anorg Allg Chem* 333: 188

6. Dahn JR, von Sacken U, Michal CA (1990) *Solid State Ionics* 44: 87
7. Ohzuku T, Ueda A, Nagayama M, Iwakoshi Y, Sawai K (1992) *Chem Express* 7: 689
8. Ohzuku T, Ueda A, Nagayama M (1993) *J Electrochem Soc* 140: 1862
9. Schäf O, Widmer T, Guth U (1997) *Ionics* 3: 277
10. Brüser V, Klingner W, Möbius H-H, Guth U (1997) Galvanic solid state sensors for potentiometric determination of CO<sub>2</sub> sensor. In: 8. Int. Sensorkongreß der AMA Conference proceedings A39: 6
11. Mohan Rao M, Solaiyan C, Deenadayalan S, Muzhumathi S, Chandrasekaran R, Pattabiraman R (1995) A novel method of preparation of gamma lithium aluminate for use as molten carbonate fuel cell matrix material. In: Proceedings of the first international symposium on new materials for fuel cell systems, Montreal, Canada
12. Kottaisamy M, Jayakumar D, Jagannathan R, Mohan Rao M (1996) *Mater Res Bull* 31: 1013
13. Kottaisamy M, Mohan Rao M, Jayakumar D (1997) *J Mater Chem* 7: 345
14. Ekambaram S, Patil KC (1995) *J Mater Chem* 5: 905
15. Aruldas N, Patil KC (1993) *J Alloys Compd* 202: 137
16. Manoharan SS, Patil KC (1992) *J Am Ceram Soc* 75: 1012
17. Dostal A, Schroder U, Scholz F (1995) *Inorg Chem* 34: 1711
18. Scholz F, Nitschke L, Henrion G (1989) *Naturwissenschaften* 76:71
19. Dostal A, Mayer B, Scholz F, Schroder U, Bond AM, Marek F, Shaw J (1995) *J Phys Chem* 99: 2096
20. Jayarama Reddy S, Dostal A, Scholz F (1996) *J Electroanal Chem* 403: 209
21. Jain SR, Adiga KC, Pai Verneker VR (1981) *Combust Flame* 40: 71
22. Dyer LD, Borie BS, Smith GP (1954) *J Am Chem Soc* 78: 1499
23. Rahner D, Machill S, Schlorb H, Siury K, Kloss M, Plith W (1998) *J Solid State Electrochem* 2: 78
24. Jayalakshmi M, Gomathi H, Prabhakara Rao G (1997) *Solar Energy Mater* 45: 201
25. Itaya K, Uchida I (1986) *Acc Chem Res* 19: 162
26. Scholz F, Meyer B (1998) Voltammetry of solid microparticles immobilized on electrode surfaces. In: Bard AJ, Rubinstein I (eds) *Electroanalytical chemistry, a series of advances*, vol 20. Dekker, New York, pp 1
27. Joseph J, Gomathi H, Prabhakara Rao G (1992) *Bull Electrochem* 8: 86