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# Electrochemical Intercalation of Oxygen in $La_2NiO_{4+x}$ ($0 \leq x \leq 0.145$)

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Previous studies have demonstrated that oxygen can be intercalated into oxides with the perovskite and $K_2NiF_4$ structures by electrochemical oxidation in aqueous KOH at ambient temperature.[1-8] For example, Mössbauer and structural measurements made on electrochemically oxidized $SrFeO_3$ clearly show that oxygen intercalation into the bulk solid can occur from solution.[2] The chemical diffusion coefficients in these electrochemical experiments[6,7] are apparently much higher ($10^{-7}$ cm$^2$/s) than would be calculated by extrapolating diffusion coefficients from high-temperature measurements on related materials ($10^{-14}$ cm$^2$/s).[9]

Previous studies of the oxides, $La_2MO_4$ (M = Co, Ni, Cu) at high temperatures have shown that oxygen ions can be intercalated into interstitial sites between adjacent octahedral layers.[10,11] Similar results have also been obtained electrochemically by oxidation of $La_2CuO_4$ and $La_2NiO_4$ at constant potential just below oxygen evolution[3,5,7,8] and also for $La_2CuO_4$ under constant-current conditions.[6,13] In one series of experiments on $La_2CuO_4$, electrochemical reduction was also investigated.[13] Very different electrochemical characteristics were observed consistent with phase separation. Measurements of superconducting transition temperatures together with the difference in electrochemical behavior on cycling suggest that electrochemically prepared oxidized samples do not reach equilibrium.[12,13]

A recent electrochemical study of the isostructural compound $La_2NiO_{4+x}$ has shown that $x$ values as high as 0.25 can be achieved.[14] The experiments were carried out by oxidation at constant potential for different times in order to synthesize a series of discrete compositions. Open-circuit voltages emphasizing the higher compositions were reported, but no data were presented for the deintercalation of oxygen on reduction and the question of the reversibility of oxygen intercalation was not addressed.[14,15] In the course of similar experiments, we have found that both oxidation and reduction of $La_2NiO_{4+x}$ are rapid and highly reversible in the composition range $0 \leq x \leq 0.145$. The electrochemical data obtained for $La_2NiO_{4+x}$ have been used to define the phase diagram, determine the thermodynamics of oxygen intercalation and to estimate the oxygen chemical diffusion coefficient in the single phase region.

$La_2NiO_{4+x}$ was prepared by a standard ceramic technique. Stoichiometric amounts of $La_2O_3$ (predried at 800 °C, Aldrich 99.9%) and NiO (Aldrich 99.99%) were ground and heated at 1250 °C. The sample was pelletized and heated to 1380 °C for 12 h. Powder X-ray diffraction data were measured with a Scintag XDS2000 diffractometer using Cu K$\alpha$ radiation in the range $10° \leq 2\theta \leq 70°$. The X-ray powder diffraction data were completely indexed by a tetragonal $K_2NiF_4$ structure with cell constants $a$ = 5.461 Å and $c$ = 12.64 Å. Thermogravimetric measurements were performed in a 5% hydrogen 95% nitrogen atmosphere to determine the oxygen content. Samples prepared by the above procedure were used in the electrochemical experiments in the following way. Pellets 8 mm in diameter and 1 mm thick (approximately 100 mg) were painted on one surface with gold paste, and a 0.025-cm-diameter platinum wire was attached to the paint. The gold film was then dried at room temperature for 3 h and annealed in air at 900 °C for 12 h. The pellets were then furnace cooled. Leads attached by this method were shown to behave ohmically by placing two such gold films on either side of a pellet and checking the $I$–$V$ characteristics. A linear relationship between current and voltage indicated proper ohmic contact. Pellets without gold paint but heat treated in the same way were analyzed thermogravimetrically and found to have a composition $La_2NiO_{4.13\pm0.02}$ for four samples.

Electrochemical experiments were performed using a Biologic MacPile potentiostat–galvanostat and a three-electrode system with the sample as the working electrode, gold foil as the counter electrode, and Hg/HgO/1 M KOH ($E_0$ = +0.098 V vs SHE) as the reference electrode. The electrolyte was 1 M KOH that had been purged with nitrogen for 3 h prior to the start of an experiment. The experiments were carried out with a continuous nitrogen purge to avoid the competing reaction of oxygen reduction that can occur at low potentials. Galvanostatic experiments were performed at a constant current of 0.1 mA (75 $\mu$A/cm$^2$) and the voltage was recorded in the range −0.4 through +0.6 V with respect to a Hg/HgO reference electrode. In a second kind of electrochemical experiment, the potential was changed in 5-mV steps from −0.4 through +0.6 V, and the current was recorded. The potential was programmed to step whenever the current dropped below 0.01 mA (7.5 $\mu$A/cm$^2$). The potential step experiment can be considered to approach an equilibrium measurement because of the very low current density at the end of each step. The current was monitored during each step.

The electrochemical results for $La_2NiO_{4+x}$ are shown in Figures 1 and 2. The potential step data imply that the initial composition of the sample is 4.145 consistent with

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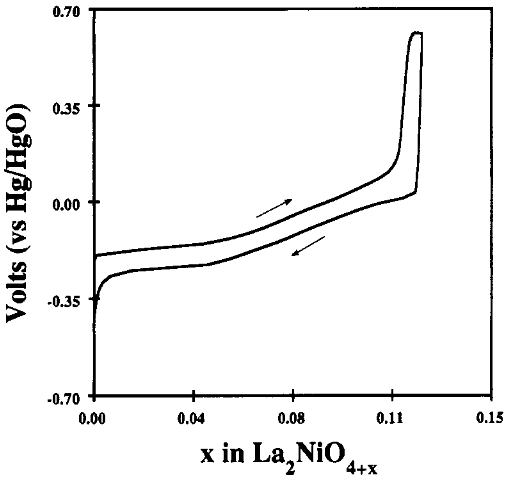

**Figure 1.** Voltage versus composition data for reduction and oxidation of $La_2NiO_{4+x}$ at constant current (75 $\mu$A cm$^{-2}$) in aqueous 1 M KOH at ambient temperature.

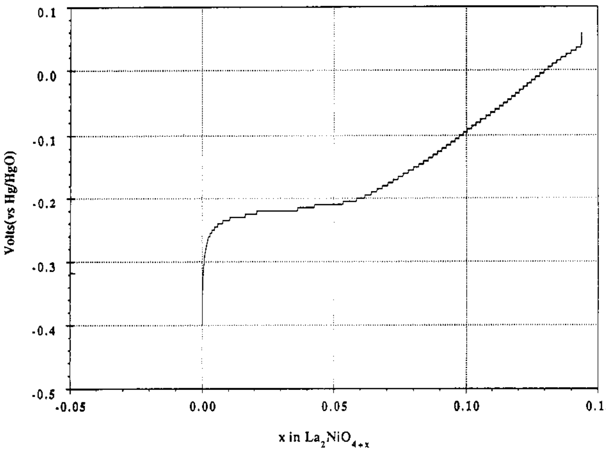

**Figure 2.** Voltage versus composition data for reduction of $La_2NiO_{4+x}$ in aqueous 1 M KOH at ambient temperature. Each voltage step is 5 mV and the cutoff current value is 10 $\mu$A.

the measured composition 4.13 ± 0.02. The data in Figure 1 indicate a slightly lower value (4.12), presumably due to the higher reaction rate used. The complete cycle shown in Figure 1 required 36 h while the potential step experiment required much longer (154 h) because of the lower effective current. Qualitatively the two experiments appear quite similar. A continuous change in potential is observed for $x$ values of $0.145 \geq x \geq 0.06$ followed by a region in which there is little change in potential with change in $x$ ($0.06 \geq x \geq 0.01$). For $x < 0.01$, the potential falls very steeply. The results indicate single-phase regions in the ranges $0.145 \geq x \geq 0.06$ and $0.01 \geq x \geq 0$, separated by a two-phase region in the range $0.06 \geq x \geq 0.01$. The phase diagram implied by these electrochemical results at 25 °C is in close agreement with the high-temperature phase diagram obtained by equilibration of single crystals at controlled oxygen fugacities.[1] X-ray patterns were obtained at $x$ values of 0, 0.03, 0.065, and 0.13. The data were recorded on pellets without grinding so that further adjustments to the composition could be made electrochemically. As a consequence, accurate determination of the lattice parameters was not possible but the results were consistent with those of Rice *et al.*[16] In particular, the orthorhombic splitting expected for $La_2NiO_{4.0}$ was clearly observed. The phase diagram is also in agreement with an TEM study performed on $La_2NiO_{4+x}$.[18]

From Figure 1 it is evident that the electrochemical intercalation of oxygen is reversible for $La_2NiO_{4+x}$. Galvanostatic charge/discharge cycles of several different pellets produced similar results. Measurement of the cell resistance suggest that the separation of the charge/discharge curves can largely be attributed to the internal resistance of the cell. The open-circuit voltages at three compositions between 0 and 0.15 obtained by Demourgues *et al.*[16] are in reasonable agreement with our potential step results. The data indicate that there is negligible polarization at the $La_2NiO_{4+x}$ electrode and that after *iR* correction the potential step data are close to the equilibrium open circuit values. Therefore, we have used the results in Figure 2, after correction for *iR* and the reference electrode potential, to extract the free energy change for the reaction

$$La_2NiO_{4+x} + \delta/2O_2 \rightarrow La_2NiO_{4+x+\delta} \quad (0.06 \leq x \leq 0.13) \tag{1}$$

By integration of the $V$ versus $x$ curve (Figure 2), the free energy change for the reaction in eq 1 was determined to be −153 kJ/(mol of $O_2$). A value for the enthalpy of oxidation can be determined from the free energy if the entropy of oxidation is known. An average value of the entropy of oxidation of −180 J/K (mol of $O_2$) was assumed.[19] Using this value, we obtain −207 kJ/(mol of $O_2$) for the enthalpy of oxidation corresponding to eq 1. This result is in excellent agreement with the value of −210 kJ/(mol of $O_2$) obtained for $La_2NiO_{4+x}$ by calorimetric measurements.[12]

From the potential step experiment, it was also possible to estimate the chemical diffusion coefficient from the current decays during each step in the one-phase region of Figure 2. Previous studies[20,21] have shown that from a potential step experiment, chemical diffusion coefficients can be calculated using the formula

$$I(t) = (Q/L)(D/\pi t)^{1/2}$$

where $Q$ is the charge transferred during the step, $L$ is the thickness, and $t$ is the time. From the slope of a plot of $I$ versus $t^{-1/2}$, a chemical diffusion coefficient can be calculated. From our data in the range $0.145 \geq x \geq 0.06$ an average chemical diffusion coefficient of about $10^{-7}$ cm$^2$/s was estimated. The diffusion mechanism and the nature of the diffusing species are not yet fully understood.

In summary, the electrochemical intercalation of oxygen into $La_2NiO_{4+x}$ in the composition range $0 \leq x \leq 0.145$ has been shown to proceed rapidly and reversibly at ambient temperature. The results are in contrast to similar data for $La_2CuO_4$ which show significant departures from equilibrium behavior.

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