

substance: NiO

property: defects in pure NiO, conductivity

defects: NiO is approximately stoichiometric at the Ni/NiO phase boundary, but at higher oxygen partial pressures, it is cation deficient, the dominant vacancies being variously-charged Ni vacancies. The deviation from stoichiometry as a function of temperature is shown in Fig. 1, and averaged values of x in Ni_{1-x}O from the literature [65F, 70V, 61M, 68S, 70T, 71O] are given by $x = 0.1093 \exp(-18525[\text{cal mol}^{-1}]/RT)$ (i.e. an activation energy of 0.804 eV). The deviation from stoichiometry in Ni_{1-x}O as calculated from diffusion data is similar to the data given in Fig. 1, varying for representative samples between $x = 0.2 \cdot 10^{-4} \dots 1.49 \cdot 10^{-4}$ at 900 K to $1.92 \cdot 10^{-4} \dots 11.70 \cdot 10^{-4}$ at 1300 K [73D]. No agreement exists over the variation of $[\text{V}_{\text{Ni}}]$ with p_{O_2} and approximations to two different power laws have been reported for $T > 1000$ K: $[\text{V}_{\text{Ni}}] \propto p_{\text{O}_2}^{1/6}$ [68S, 69T] and $[\text{V}_{\text{Ni}}] \propto p_{\text{O}_2}^{1/5}$ [70T]. The former would correspond to doubly ionized Ni vacancies as the predominant defects whereas the latter will correspond to a mixture of defects. It can be shown [71O, 73D] that the power law and the parameters derived from a point defect model will be extremely sensitive to the presence of small quantities of compensating donors.

conductivity

Ionic conductivity remains very small; at 1000°C in air, $t_{\text{Ni}^{2+}} \approx 2 \cdot 10^{-7}$ [79D].

At high temperatures ($T \geq 1200$ K) σ varies with p_{O_2} (Fig. 2). No precise power law has been derived. Widely different exponent values have been published, though a $p_{\text{O}_2}^{1/5}$ law at high temperatures seems to be favoured:

parameter n in a power law $\sigma \propto p_{\text{O}_2}^{1/n}$

oxygen pressure region (p in atm)			
n			
5.57	$T = 1100^\circ\text{C}$	$1 \dots 10^{-4}$	71O
5.74	$T = 1200^\circ\text{C}$		
5.76	$T = 1300^\circ\text{C}$		
5.65	$T = 1400^\circ\text{C}$		
3.97	$T = 950^\circ\text{C}$	$1 \dots 10^{-4}$	69E
4.08	$T = 1000^\circ\text{C}$		
4.17	$T = 1050^\circ\text{C}$		
4.26	$T = 1100^\circ\text{C}$		
4.27	$T = 1150^\circ\text{C}$		
4.44	$T = 1200^\circ\text{C}$		
4.8	$T = 950^\circ\text{C}$	$1 \dots 10^{-2}$	73D
5	$T = 1000^\circ\text{C}$		
4.8	$T = 1050^\circ\text{C}$		
4.8	$T = 1100^\circ\text{C}$		
5.1	$T = 1150^\circ\text{C}$		
4.9	$T = 1200^\circ\text{C}$		
4.6	$T = 1050^\circ\text{C}$	$1 \dots 10^{-5}$	70V
4.8	$T = 1205^\circ\text{C}$		
5	$T = 1245^\circ\text{C}$		
5.3	$T = 1377^\circ\text{C}$		
6	$T = 1300^\circ\text{C}$	$1 \dots 10^{-6}$	61M
4.6	$T = 1500^\circ\text{C}$	$1 \dots 10^{-6}$	68B
4.2	$T = 1400^\circ\text{C}$		
4.1	$T = 1300^\circ\text{C}$		
4.2	$T = 1200^\circ\text{C}$		
4.05	$T = 1100^\circ\text{C}$		
4	$T = 1000^\circ\text{C}$		
4.28...4.30	$T = 1000^\circ\text{C}$	$1 \dots 1.89 \cdot 10^{-4}$	78F
4.27...5.18	$T = 1200^\circ\text{C}$		
4.40...5.88	$T = 1400^\circ\text{C}$		
4.6	$T = 1050^\circ\text{C}$	$1 \dots 10^{-3}$	74I

4.5	$T = 1000^{\circ}\text{C}$		
4	$T = 900^{\circ}\text{C}$	$1 \dots 10^{-6}$	79D
4.7	$T = 1000^{\circ}\text{C}$		
4.8	$T = 1100^{\circ}\text{C}$		
5.1	$T = 1200^{\circ}\text{C}$		
5.4	$T = 1250^{\circ}\text{C}$		

activation energies for conductivity

high-temperature region, data at constant partial pressure of oxygen (normally in air)

		$T [^{\circ}\text{C}]$, $p [\text{atm}]$		
E_A	1.07(1) eV	1182...1762, $1 \dots 5 \cdot 10^{-7}$	$\sigma = 65(11) \cdot 10^6 [\Omega^{-1} \text{ cm}^{-1}] \exp(-E_1/RT)$, $E_1 = 36.4(6) \text{ kcal mol}^{-1}$ in pure CO_2 ; $\sigma = 7.5 \cdot 10^6 [\Omega^{-1} \text{ cm}^{-1}] \exp(-E_A/kT)$ in pure O_2 ; single crystal	70V
	1.00 eV	1000...1250, $1 \dots 10^{-3}$	single crystal, ac data	67U
	0.92(2) eV	1000...1600, $1 \dots 10^{-6}$		68B
	0.94...1.10 eV	900...1200, $1 \dots 10^{-4}$	single crystal	69E
	0.81 eV	900...1400, $1 \dots 10^{-4}$	single crystal and ceramic	71O
	0.86 eV	900...1300, $1 \dots 10^{-4}$	single crystal and ceramic	73D
	1.01 eV		see Fig. 3 for further values	79D
	0.3 eV	$T_N \dots 730$	single crystal, air	78K
	0.3 eV	$T_N \dots 690$	polycrystalline air	73N
	0.40.8 eV	$T > T_N$	air	66V
lower temperature region				
E_A	0.69 eV	$-20 \dots 130$	flame-fusion-grown crystal, see Fig. 4, dry nitrogen	68A1
	0.5...0.7 eV	$20 \dots 130$	air	66V
	0.6...0.9 eV	$130 < T < T_N$	air	
	$\approx 0.6 \text{ eV}$	$T < T_N$	single crystal, air	78K
	$\approx 0.6 \text{ eV}$	$T < T_N$	polycrystalline material, air	73N

The similarity of the high-temperature activation energies for conduction and defect formation suggests that μ is not activated in this temperature region [71O]. This conclusion is supported by the Seebeck data, which approximately tracks the conductivity (Fig. 5). Combined thermogravimetric and conductivity data give a drift mobility of $0.53 \text{ cm}^2/\text{V s}$ in the temperature range $1000\ldots1400^\circ\text{C}$ [69T, 70T, 71O]. The constancy of this result is not supported by other work; [61M] suggests an activation energy for mobility of 5.5 kcal/mol in this region, close to that expected from a $T^{3/2}$ impurity scattering law. Work on very high purity crystals [78K] suggests that the Seebeck and conductivity activation energies do not track at all in the range $\text{RT}\ldots1000 \text{ K}$ but the discrepancy becomes markedly worse below T_N with the activation energy rising to 0.6 eV compared to 0.2 eV for the Seebeck coefficient (which does not change at T_N). This conclusion is suggested also by [68B] who find an activation energy for σ of 0.92 eV and for the thermopower of 0.66 eV at $1000\ldots1600^\circ\text{C}$.

conduction mechanism at lower temperatures

ac conductivity shows a marked dispersion at low temperatures (Fig. 6) suggesting the hopping of bound carriers (hopping energy: 0.7 eV) [68A1].

References:

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Fig. 1.

Ni_{1-x}O . Stoichiometry x vs. (reciprocal) temperature at 1 and 10^{-3} atm O_2 , curve 1 [61M], 2 [68S], 3 [69T].

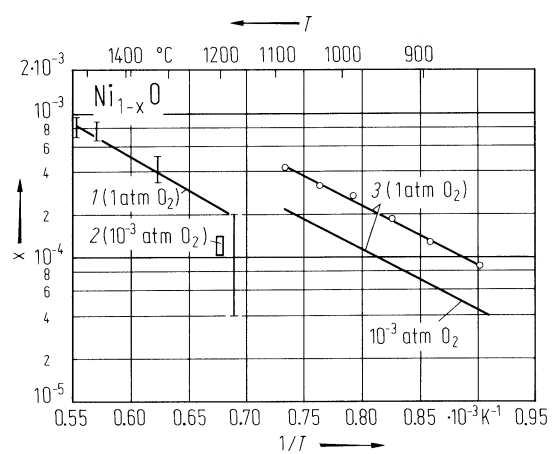


Fig. 2.

NiO. Electrical conductivity vs. oxygen partial pressure for various temperatures [68B].

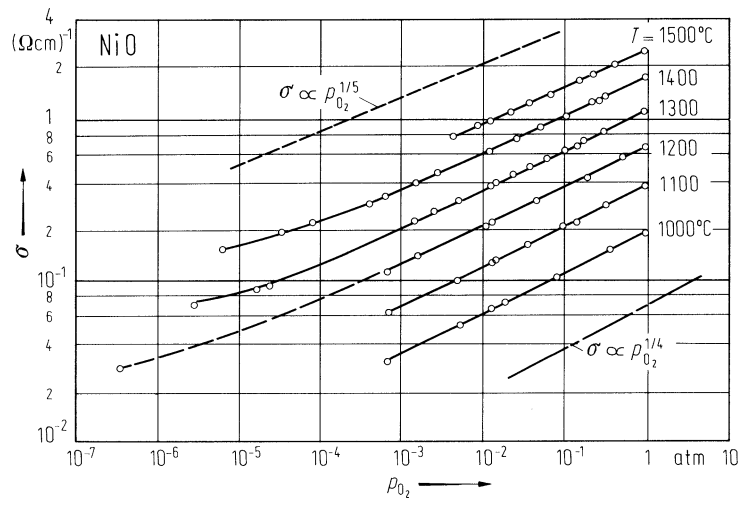


Fig. 3.

NiO. High temperature conductivity vs. reciprocal temperature. Data from two authors [79D].

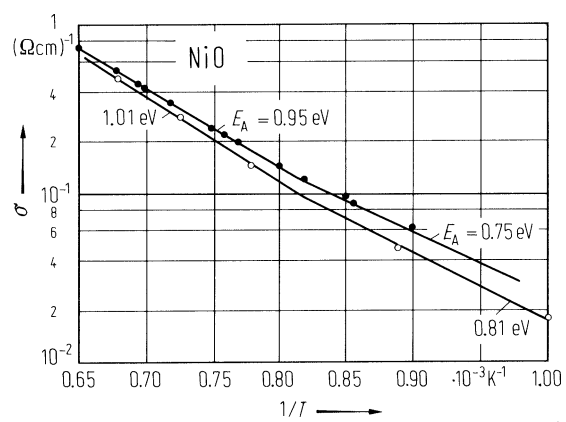


Fig. 4.

NiO. dc conductivity vs. reciprocal temperature for single crystals containing excess oxygen [68A1]. Flame fusion: crystal grown by flame fusion techniques; annealed F.F.: flame fusion grown crystal annealed in O_2 at 1050°C for two days; halide decomposition: crystal grown by decomposition of $NiBr_2$ in gas phase transport.

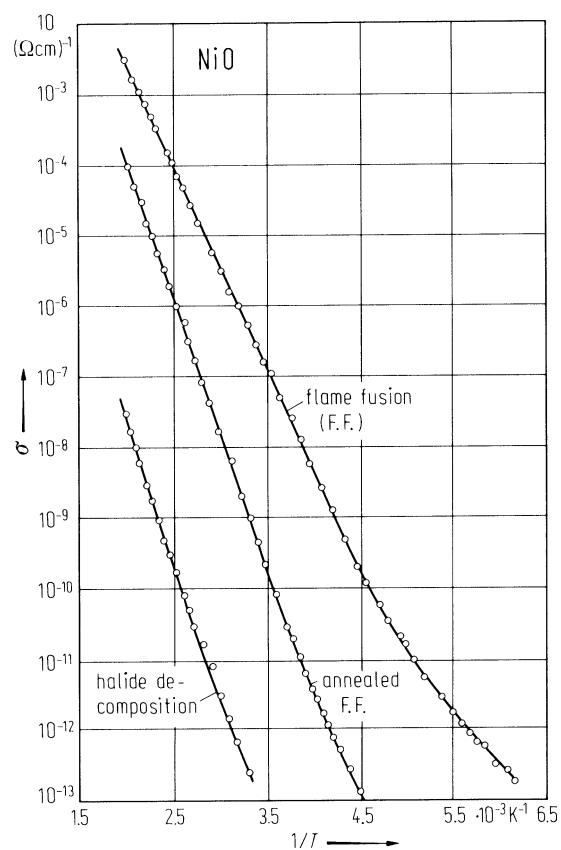


Fig. 5.

NiO. Reduced Seebeck coefficient and conductivity vs. reciprocal temperature of polycrystalline material (prepared from spectroscopically pure powder) at 10^{-1} atm oxygen [71B].

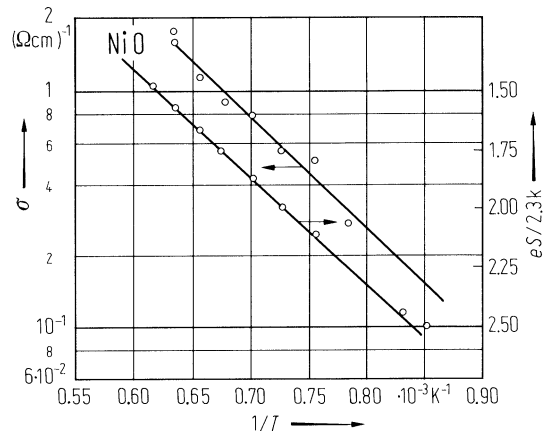


Fig. 6.

NiO. dc conductivity and real part of the ac conductivity vs. reciprocal temperature at fixed frequencies [68A2].

