Redox-induced proton insertion and desertion of zircon-type neodymium chromate(V)

Yoshitaka Aoki^{*,a, b}, Kosuke Kuroda^a, Etsushi Tsuji^a and Hiroki Habazaki^a

a Faculty of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo, 060-8628 Japan. *b*

PRESTO, Japan Agency of Science and Technology, Saitama, 332-0012 Japan.

Corresponding: Yoshitaka Aoki

Tel : +81-11-706-6752

E-mail : y-aoki@eng.hokudai.ac.jp

Key word: high valence state oxide, proton insertion reaction, PCFC

Abstract

Redox transformation of $\text{NdCr}^{\text{V}}\text{O}_4$ involved by insertion/desertion of protons was examined by XRD, XPS, *in situ* FT-IR and fuel cell tests. It was found that NdCrO_4 caused bulk reduction with H_2 gas at around 400°C , changing to amorphous Nd(III)-Cr(III) hydroxide phase. This hydroxide phase, however, could recover to the original zircon type oxide phase by air oxidation at the same temperature region. Proton-conducting ceramic fuel cells having NdCrO_4 film as an interlayer between cathode and electrolyte was fabricated and the cell was confirmed to exhibit remarkable power generation giving rise to OCV of more than 1.0 V at 500°C . It was speculated that the interlayer facilitates proton transfer from electrolyte to cathode because redox cycling of NdCrO_4 and the corresponding hydroxide was driven by the high proton chemical potential at the interface with electrolyte and plenty of oxygen in cathode gases.

Introduction

Reactivity of transition metal oxides consisting of high valence state metal ions, such as Cr^{V} , Fe^{VI} , Co^{IV} , Cu^{III} and so on has been focus of the many investigations because of its roles in super ion battery [1,2], biological reactions [3-5] and heterogeneous catalytic processes [6-8]. The unusual reactivity of these metal oxides is due primarily to the relatively high redox potential of high valence state metal ions. Rare earth chromates, RECrO_4 (RE: rare earth metal(III)), are a group of compounds comprising from tetrahedral $\text{Cr}^{\text{V}}\text{O}_4^{3-}$ oxoanions, and are thermally stable at temperatures below 600°C in ambient atmosphere [9,10]. Previously, we reported that zircon-type NdCrO_4 undergoes unique redox reaction with gaseous alcohol, accompanied by insertion and desertion of protons into the solids [11,12]. It was reduced with methanol gases at around 270°C , changing to the low-crystalline, Cr(III) hydroxide phase by attracting hydrogen atoms from methanol [11, 12]. The hydroxide phase, however, was easily oxidized in air at the same temperature to recover to the original NdCrO_4 phase [11]. This unique reactivity may disclose that NdCrO_4 possesses bulk diffusivity of proton and electron. Such a mixed proton and electron conducting material is rather rare [13,14], but is attractive as reversible electrode materials for hydrogen rechargeable battery, hydrogen pump devices and so on. Thus it is of fundamental and of technological interest to understand this unique behavior of the Cr(V) oxides.

Calcium chromate, $\text{CaCr}^{\text{VI}}\text{O}_4$, is hexavalent chromium oxide, having the same crystal structure as $\text{NdCr}^{\text{V}}\text{O}_4$. Standard redox potential of $\text{Cr}(\text{VI} \rightarrow \text{III})$ (1.33 V vs NHE) [15] is almost same as that of $\text{Cr}(\text{V} \rightarrow \text{III})$ (1.32 V vs NHE) [3]. Hence, CaCrO_4 is a good target to

evaluate the reactivity of NdCrO_4 by comparison method. Herein, we examined the redox behavior of these two high valence state chromates through the reactions with H_2 gas. Bulk reduction does not take place in CaCrO_4 because the poor electrical conductivity and relatively small free volume do not allow the enhanced diffusion of electron and proton. Moreover, it is demonstrated redox cycling of NdCrO_4 and the corresponding hydroxide form proceeds under cathodic conditions of operating proton-conducting ceramics fuel cell (PCFC). The unique reactivity may attribute to the coexistence of the relatively large interstitial spaces and singular Cr(V) oxidation state in NdCrO_4 .

Experimental

Synthesis method of a single phase zircon-type NdCrO_4 was described elsewhere [16]. Zircon-type CaCrO_4 samples were also prepared by the similar method. In briefly, $\text{Nd}(\text{CH}_3\text{COO})_3$ (99.9% purity, Kanto) or $\text{Ca}(\text{CH}_3\text{COO})_2$ (99.9% purity, Kanto) and CrO_3 (99.9% purity, Kanto) powders were dissolved into Milli-Q water at a stoichiometric Nd/Cr or Ca/Cr molar ratio. The solutions were heated at 140°C in order to evaporate water and then once heated at 400°C for 1 h in air, and thus the precursor powders were obtained. For NdCrO_4 , the precursor was calcined at 580°C for 3 h in air. In case of CaCrO_4 , the precursor was calcined at 750°C for 3 h in air. The purity of the samples was determined by chemical titration, XPS, and XRD. The specific surface area of the sample powder was measured by nitrogen adsorption (BET method) at -198°C . The reaction of NdCrO_4 with H_2 was carried out in a continuous-flow tubular fixed-bed reactor of a quartz tube (7.0 mm in diameter); 100 mg

of sample powder was used as the reactant. Before the reaction, the temperature of the sample was raised at $10^{\circ}\text{C min}^{-1}$ in the ambient atmosphere, and maintained at $250\text{--}500^{\circ}\text{C}$ for 1 h under an Ar (99.99 % pure) flow $100\text{ cm}^3\text{ min}^{-1}$. The reaction was started by flowing pure hydrogen gas at $100\text{ cm}^3\text{ min}^{-1}$. The samples after the reduction were isothermally oxidized in the same reactor by switching the flow of hydrogen to dry air.

The XRD patterns were measured by the Rigaku diffractometer with a monochromator. The XPS measurements were carried out by a JEOL JPS-9010MC. Fourier-transform infrared (FT-IR) spectra were recorded in a diffuse reflectance mode by using a JASCO FT/IR-350 spectrometer. The *in situ* FT-IR measurements were conducted with a gas-sealed optical cell with an antireflective glass window to acquire the spectra under the controlled atmosphere and temperature. The cell was smaller than 10 cm^3 and equipped with an electronic furnace. Thermogravimetry (TG) was conducted by using a Shimadzu DTG-30A.

Proton conducting ceramic fuel cells (PCFC) having NdCrO_4 cathode interlayer were fabricated. $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) was prepared by a solid state reaction method. Stoichiometric amounts of high-purity barium carbonate, zirconium oxide, cerium oxide, and yttrium oxide powders (all from Kanto Chemicals) were mixed and calcined at 1050°C in air for 10 h to form the perovskite phase. After confirming a single phase by XRD, the ceramic powders were pressed into pellets by CIP at 100 MPa and sintered at 1500°C in air for 20 h to form a dense BZCY pellet ($> 85\%$ of ideal density) as an electrolyte. Pt paste was applied on one face as anode and fired at 800°C for 1 h to form porous Pt electrodes. Porous layer of NdCrO_4 paste prepared by mixing the as-prepared powders and α -terpineol (Aldrich) was

screen printed on the another face of BZCY electrolyte and, subsequently, porous layer of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) paste (Alsrich) was screen printed as a cathode and annealed at 600 °C for 1 h. Thus, a single cell consisting of a Pt anode (100 nm), a BZCY electrolyte film (1 mm), NdCrO_4 cathode interlayer (10 μm) and a LSCF cathode (20 μm) was obtained. The electrode active area was 0.283 cm^2 . Two gold wires were connected to each electrode as current leads. The cell was mounted on an alumina supporting tube for fuel-cell testing at 400–700 °C with humidified hydrogen (3 vol% H_2O) as fuel and stationary air as oxidant. The fuel-cell performances were measured using a Solartron Potentiostat/Galvanostat (Model 1283A).

Results and Discussion

Figure 1a shows XRD patterns of NdCrO_4 powders (specific surface areas of 4.0 $\text{m}^2 \text{g}^{-1}$) reacted with H_2 gas for 20 min at elevated temperatures. Zircon type structure of NdCrO_4 is deformed by reacting with H_2 gas at temperatures above 380°C. The XRD patterns still retains the features of zircon type phase in addition to a broad halo peak of amorphous phase at around 33° after 20 min reaction with H_2 at 380°C, but the longer reduction further deteriorates the zircon structure and develops the amorphous state (Fig. 1b). **Figure 1d shows a TEM image of NdCrO_4 specimens and the corresponding selected-area electron diffraction (SAED) patterns from different particles, revealing crystalline and amorphous phases coexist in the reduced for 20 min (Fig. 1d). These features clearly show that NdCrO_4 phase transforms to amorphous state by reduction with H_2 at 380°C.**

Cr 2p XPS spectra reveal Cr(V) ions are reduced to Cr(III) state after the 20 min reaction at 380°C (Fig. 2a). The $2p_{3/2}$ peak position of as-prepared NdCrO₄ (578.5 eV) is in agreement with the values of the Cr(V) oxides [16]. The $2p_{3/2}$ peak clearly shifts to lower energy side and is located at around 576.3 eV after the reaction. This value is similar to that of the Cr(III) oxides Cr₂O₃ (576.6 eV) [17]. NdCrO₄ is reduced with H₂ at 380°C.

Figure 3a shows a TG curve of NdCrO₄ samples, measured in pure H₂ gas. It keeps the weight below 400°C but abruptly losses 8% weight at around 450°C as transforming to perovskite-type NdCrO₃ by releasing one oxygen atom a molecular. NdCrO₄ must show 0.77 wt% mass gain if it is reduced by the following hydrogenation reaction.

When it is exposed to H₂ atmosphere at 380°C, the weight of NdCrO₄ is logarithmically increased and the reaction is in stationary after 1800 s so as to gain about 0.6 wt% (Fig. 3b). This value is close to the mass gain by Eq. 1. In conclusion, the charge loss by chromium reduction is compensated by proton insertion into the NdCrO₄ lattice instead of losing the lattice oxygen at the temperatures below 400°C.

The amorphous phase prepared by 1 h reduction at 380°C is reversibly changed to zircon phase by isothermal oxidation in air (Fig. 1b). Sharp XRD peaks of zircon-type phase are recovered after 10 min oxidation, indicating that the degraded structure was quickly restored by oxidation.

In situ FT-IR spectroscopy clearly reveals evolution of hydroxyl groups in NdCrO₄ by hydrogen reduction (Fig. 4a). The sharp peak near 3350 cm⁻¹ is the noise from detector. The

broad IR peaks at around 3500 cm^{-1} are assigned to the stretching mode of hydroxyl group (-OH). The -OH group immediately develops as exposing to H_2 gas and the peak intensity is continuously increasing for 10 min. These features reveal that NdCrO_4 phase is converted to the Cr(III) hydroxide phase by incorporation of protons. When the hydroxide is exposed to air at the same temperature, the hydroxyl groups are rapidly degraded by air oxidation and are completely removed in 4 min. Based on the results by XRD, TG and FT-IR, NdCrO_4 bulk is reduced by H_2 gas at 380°C as changing to amorphous Nd(III)-Cr(III) hydroxide phase and the hydroxide is easily oxidized in air and reversibly returns to the zircon type oxide by losing hydrogen atoms.

Zircon type $\text{CaCr}^{\text{VI}}\text{O}_4$ is thermally stable at temperatures below 800°C in air [18]. The lattice parameters of CaCrO_4 ($a = 0.7222\text{ nm}$, $c = 0.62851\text{ nm}$) [19] are close to those of NdCrO_4 ($a = 0.73107\text{ nm}$, $c = 0.63999\text{ nm}$) [16]. In addition, a standard redox potential of Cr^{V} and Cr^{VI} ions is quite similar each other, as mentioned before. Nevertheless, bulk reduction of CaCrO_4 does not occur even at 500°C . CaCrO_4 retains its original zircon-type structure after exposing to H_2 gas for 1 h at 500°C (Fig. 1c). Redox titration shows that the average oxidation state of Cr in the reduced at 500°C for 1 h is almost 6+. Meanwhile, Cr 2p XPS of CaCrO_4 shows $2p_{3/2}$ peaks at around 580 eV, which is in agreement with the value for Cr(VI) oxides [20], but the peak shifts to 576 eV after 1 h reduction at 400°C . Apparently, the surface of CaCrO_4 is reduced by $\text{Cr(VI)} \rightarrow \text{Cr(III)}$ (Fig. 2b). Fig. 4b is the *in situ* FT-IR spectra measured during the reduction and re-oxidation cycle. The peak at around 3650 cm^{-1} is assigned to the second overtone of CrO_4^{2-} stretching band. The hydroxyl groups quickly

develop by reacting with H_2 as is the case with $NdCrO_4$, but the peak intensity of $-OH$ stretching does not change after 1 min reduction. In addition, the hydroxyl groups are completely removed by 1 min oxidation. These results indicate that the reduction is terminated by forming the surface $Ca(II)$ - $Cr(III)$ hydroxide layer. In $CaCrO_4$, the inner diffusion of electron and proton does not occur.

The reversible transformation behavior of $NdCrO_4$ highlights the feature that the amorphous $Nd(III)$ - $Cr(III)$ hydroxide phase is more stable than zircon-type $NdCr(V)O_4$ under high hydrogen chemical potential gradients probably due to the high redox potential of Cr^V ions but the latter is more stable than the former in oxygen atmosphere at elevated temperatures. It is evident that the coupled electron and proton diffusion in $NdCrO_4$ lattice is essential to drive these bulk reactions. Previously, we reported that $NdCrO_4$ exhibited *n*-type semiconductor characteristics in ambient atmosphere, having the conductivity σ of $10^{-1} \text{ S cm}^{-1}$ order at 400°C [21]. Main electron carriers are originated from d^1 electron configuration $Cr(V)$ state. On the other hand, $CaCrO_4$ is reported to be poor electrical conductor, having σ of $10^{-5} \text{ S cm}^{-1}$ order at 400°C due to the d^0 electronic configuration of $Cr(VI)$ valence state [22]. Such difference in the electronic conductivity must attribute to the distinct reactivity between $NdCrO_4$ and $CaCrO_4$.

It has been reported that intermetallic Laves compounds RM_2 compounds (R = a rare earth metal and $M = Fe, Co, Ni$) are hydrogenated to amorphous RM_2H_x ($x \sim 4$) phase (Hydrogen-induced amorphization, HIA) [23, 24]. If the radii of the tetrahedral holes occupied by H atoms in RM_2 , r_h , are larger than the critical value (0.04 nm), RM_2 tends to be

hydrogenated. However, the RM_2 with r_h of less than the threshold is not hydrogenated (and thus do not cause HIA) because the tetrahedral site is small for the occupation by hydrogen atoms. Protons may occupy an interstitial site in NdCrO_4 as is the case with other zircon-type oxides [25], although it is difficult to define precisely the site in zircon-type phase. The free volume of NdCrO_4 and CaCrO_4 are calculated by using lattice constants and ionic radius [26] to be 51% and 46%, respectively. Accordingly, it is plausible that NdCrO_4 with relatively large free volume is hydrogenated to amorphous hydroxides because it possesses large interstitial spaces for proton occupation. On the other hand, it is speculated the hydrogenated CaCrO_4 is not thermodynamically stable due to the relatively small interstitial space and thus the bulk reduction is not progressive.

In the reduction of NdCrO_4 , protons diffuse inward across the amorphized, hydroxide layer, so that the diffusivity of this layer may limit the rate of proton insertion. However, the protons must diffuse inside the restored NdCrO_4 lattice during re-oxidation in order to release proton and electron for the water forming reaction at the surface. The restoration to zircon phase by oxidation is rather fast, indicating that NdCrO_4 exhibits fast proton conduction in ambient atmosphere.

The gas concentration cell experiments are a powerful technique to determine the transport number of ion and electron carriers. Unfortunately, it is difficult to obtain the dense pellets with gas-tightness and durability for the electrochemical measurements, because NdCrO_4 is easily pyrolyzed to perovskite-type NdCrO_3 at temperatures above 600°C even in air [16]. In order to clarify the proton diffusivity, we examined here the proton conducting ceramic fuel

cell (PCFC) with a NdCrO_4 interlayer between $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_3$ (BZCY) electrolyte and $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (LSCF) cathode. Such a cell may generate electricity, if the NdCrO_4 interlayer enables proton transfer from BZCY electrolyte to LSCF cathode.

Figure 5 shows a cross-section SEM of the NdCrO_4 film formed on a Si wafer by screenprinting with as-prepared paste. The layer consists of the oxide grains with a length of several hundred nanometers and is uniformly formed over the surface with a thickness of about $\sim 10\text{ }\mu\text{m}$. Figure 6 shows the fuel cell performance at 500°C for the cell with NdCrO_4 inter layer prepared by the same method. The cell without NdCrO_4 interlayer shows the open circuit voltage (OCV) of 1.1 V and the maximum power density of 13 mW cm^{-1} . The current voltage curve is almost linear, indicating that the limited power density of our cell is due to the large ohmic loss at the relatively thick electrolytes.

NdCrO_4 cell poses remarkable power generation at 500°C , giving the OCV of 1.1 V and the peak power density of 11 mW cm^{-2} . In a separate experiment, the cells with NdCrO_4 interlayer and Au current collector electrode at cathode side were fabricated by similar method. The cell did not give an apparent OCV, indicating that NdCrO_4 cannot electrocatalyze the oxygen reduction reaction (ORR). The ORR must proceed predominantly at LSCF in a $\text{Pt|BZCY|NdCrO}_4/\text{LSCF}$ cell. These results suggest that NdCrO_4 interlayer mainly contribute to pump out protons from electrolyte to TPB boundary. The performance of the NdCrO_4 cell is quite similar to that of the cell without NdCrO_4 interlayer, disclosing that the resistance for the proton migration in NdCrO_4 layer is not rate limiting in the current cell setup.

Previously, we conducted acceptor-doping into NdCrO_4 by Ca substitution of Nd sites, where the lack of positive charge was compensated by forming electron hole carriers, namely oxidation of Cr(V) to Cr(IV) [27]. Accordingly, it is difficult to consider as-prepared NdCrO_4 have protonic carriers generated by acceptor impurities. Thus, the protonic carriers in the interlayer is given by the reduction-induce proton insertion (Eq. 1). NdCrO_4 near BZCY electrolyte might be converted to the Cr(III) hydroxide phase owing to the high H^+ concentration gradients formed at the interface with electrolyte. However, the hydroxides are immediately oxidized to the original oxide phase under the oxygen-rich atmosphere at cathode. In the re-oxidation process, proton and electrons are released from the hydroxide/oxide reaction front and they will diffuse in NdCrO_4 matrices towards air-LSCF- NdCrO_4 three phase boundary (TPB) for water forming reaction. Hence protons are pumped out from electrolyte to cathode as the reduction and re-oxidation cycle is progressive during fuel cell operation

Current results mentioned above are not surprising in view of structural and electrochemical features of NdCrO_4 . Amezawa et al has reported that zircon-type Ca-dope YPO_4 reveals proton conductivity in wet atmosphere [28]. H^+ carriers involved by acceptor-doping can migrate within the lattice by thermally-activated jump from one phosphate anion to the neighbor. NdCrO_4 with relatively large free volume is speculated to have the similar pathway for proton carriers. As mentioned above, the redox potential of $\text{Cr(V)} \rightarrow \text{III}$ is 1.32 V vs NHE and is higher than that of the oxygen reduction potential (1.23 V vs NHE). This feature may enable reduction to Cr(III) hydroxide phase under cathodic potential

of operating fuel cell.

Conclusion

In summary, NdCrO_4 causes bulk reduction through the reactions with H_2 gas at around 400°C , changing to amorphous Nd(III)-Cr(III) hydroxide phase by proton incorporation. This hydroxide phase can recover to the original zircon type oxide phase by air oxidation at the same temperature region. The mixed proton and electron conductivity of NdCrO_4 phase is essential to the bulk redox reactions. Therefore, poor electrical conducting CaCrO_4 does not show such bulk reduction although the crystal structure and the redox potential are very similar to those of NdCrO_4 . NdCrO_4 film deposited on a BZCY electrolyte undergoes the redox cycling under the cathodic conditions of operating PCFC, because NdCrO_4 moieties near the interface with electrolyte change to the corresponding hydroxide phase by the high proton concentration gradient but the formed hydroxide is immediately re-oxidized to NdCrO_4 as accompanied by inner diffusion of electron and proton towards gas-LSCF- NdCrO_4 TPB. Hence, the PCFC having NdCrO_4 interlayer between cathode and electrolyte can give remarkable power generation at 500°C giving OCV of more than 1.0 V. The unique reactivity of NdCrO_4 is attributed to the coexistence of large interstitial space for hydrogen occupation and singular electronic states of the Cr^{V} ion in NdCrO_4 .

Acknowledgement

This work was supported by PRESTO-JST ‘Creation of Innovative Core Technology for Manufacture and Use of Energy Carriers from Renewable Energy’.

,

References

1. S, Licht and R. T.-Vered, Chem. Commun. 40 (2004) 628.
2. S, Licht, B. Wang and S. Ghosh, Science 285 (1999) 1039.
3. M. C. Ghosh and E. S. Gould, J. Am. Chem. Soc. 115 (1993) 3167.
4. E. Gould, Acc. Chem. Res. 19 (1986) 66.
5. S. I. Brauer and K. Wetterhahn, J. Am. Chem. Soc. 113 (1991) 3001.
6. B. M. Weckhuysen, I. E. Wachs and R. A. Schoonheydt, Chem. Rev. 96 (1996) 3327.
7. M. W. Kanan, J. Yano, Y. Surendranath, M. Dinca, V. K. Yachandra and D. G. Nocera, J. Am. Chem. Soc. 132 (2010) 13692.
8. J. Hu, T. Xing, Q. Jia, H. Hao, D. Yang, Y. Guo and X. Hu, Appl. Catal. A 306 (2006) 29.
9. R. Saéz-Puche, E. Jiménez, J. Isasi, M.T. Fernández-Díaz and J.L. García-Munózc, J. Solid State Chem. 171 (2003) 161.
10. E. Jiménez, J. Isasi and R. Saéz-Puche, J. Alloys Comp. 312 (2000) 53.
11. Y. Aoki, H. Habazaki and H. Konno, Chem. Mater. 15 (2003) 2419.
12. Y. Aoki, H. Habazaki and H. Konno, Chem. Lett. 33 (2004) 992.
13. A. Unemoto, A. Kaimai, K. Sato, K. Yashiro, H. Matsumoto, J. Mizusaki, K. Amezawa and T. Kawada, Solid State Ionics 178 (2008) 1663.
14. H. Matsumoto, T. Shimura, T. Higuchi, H. Tanaka, K. Katahira, T. Otake, T. Kudo, K. Yashiro, A. Kaimai, T. Kawada and J. Mizusaki, J. Electrochem. Soc. 152 (2005) A488.
15. A. J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel

Dekker, New York, 1985.

16. Y. Aoki, H. Konno, H. Tachikawa and M. Inagaki, Bull. Chem. Soc. Jpn. 73 (2000) 1197.
17. T. P. Moffat and R. M. Ratanision, J. Electrochem. Soc. 139 (1992) 1869.
18. K. T. Adendorff, J. P. R. de Villiers and G. J. Kruger, J. Am. Ceram. Soc. 75 (1992) 1416.
19. L. Li, W. Yu, Y. Long and C. Jin, Solid State Commun. 137 (2006) 358.
20. D. Shuttleworth, J. Phys. Chem. 84 (1980) 1629.
21. Y. Aoki, H. Konno and H. Tachikawa J. Mater. Chem. 11 (2001) 1214.
22. I. Yasuda and M. Hishinuma, Solid State Ionics 78 (1995) 109.
23. K. Aoki, X-G. Li and T. Matsumoto, Acta Metall. Mater. 40 (1992) 1717.
24. K. Aoki, T. Yamamoto and T. Matsumoto, Scripta Metall. 21 (1987) 27.
25. I. Saadoune, J. A. Purton and N. H. de Leeuw, Chem. Geo. 258 (2009) 182.
26. R. D. Shannon and C. T. Prewitt, Acta Crystallogr. B25 (1969) 925.
27. Y. Aoki and H. Konno, J. Solid State Chem. 156 (2001) 370.
28. K. Amezawa, Y. Tomii and N. Yamamoto, Solid State Ionics, 162-163 (2003) 175.

Figure captions

Fig. 1 (a) XRD patterns of NdCrO_4 kept at various temperatures for 20 min in H_2 atmosphere. (b) XRD patterns of NdCrO_4 specimens reduced at 380°C in H_2 and re-oxidized at 380°C in air in various reaction times. Red patterns show the reduced specimens and blue ones the re-oxidized. (c) XRD patterns of CaCrO_4 kept at various temperatures for 1 h in H_2 atmosphere. (d) TEM of NdCrO_4 powder reduced at 380°C for 20 min in H_2 . Inset is the corresponding SAED patterns at the points in TEM image.

Fig. 2 Cr 2p XPS spectra of (a) NdCrO_4 and (b) CaCrO_4 . Black spectra show the as-prepared and Red the reduced in H_2 at 380°C for 20 min with NdCrO_4 and 400°C for 1 h with CaCrO_4 .

Fig. 3 (a) Thermal gravimetry of NdCrO_4 measured in H_2 by raising temperature at $10^\circ\text{C min}^{-1}$ in the range of 25 to 1000°C . (b) Weight transient curve of NdCrO_4 kept in H_2 at 380°C . The atmosphere is switched from pure Ar to H_2 at the point indicated by blue dashed line.

Fig. 4 *In situ* FT-IR of (a) NdCrO_4 and (b) CaCrO_4 during reduced at 380°C in H_2 and re-oxidized at 380°C in air after 30 min reduction. In (a) and (b), Red spectra show the reduced and blue ones the reoxidized. Numbers beside the panels show reduction and re-oxidation time. The sharp peak near 3350 cm^{-1} is the noise from detector. In (b), the peak at around 3650 cm^{-1} is assigned to the second overtone of CrO_4^{2-} stretching band.

Fig. 5 Cross-section SEM of NdCrO_4 layer deposited on Si wafer by screen-printing method.

Fig. 6 Fuel cell performances of PCFC with a NdCrO_4 interlayer (red) and without the interlayer (black) at 500°C .

Fig. 1 (a) XRD patterns of NdCrO₄ kept at various temperatures for 20 min in H₂ atmosphere. (b) XRD patterns of NdCrO₄ specimens reduced at 380°C in H₂ and re-oxidized at 380°C in air in various reaction times. Red patterns show the reduced specimens and blue ones the re-oxidized. (c) XRD patterns of CaCrO₄ kept at various temperatures for 1 h in H₂ atmosphere. (d) TEM of NdCrO₄ powder reduced at 380°C for 20 min in H₂. Inset is the corresponding SAED patterns at the points in TEM image.

Fig. 2 Cr 2p XPS spectra of (a) NdCrO₄ and (b) CaCrO₄. Black spectra show the as-prepared and Red the reduced in H₂ at 380°C for 20 min with NdCrO₄ and 400°C for 1 h with CaCrO₄.

Fig. 3 (a) Thermal gravimetry of NdCrO₄ measured in H₂ by raising temperature at 10°C min⁻¹ in the range of 25 to 1000°C. (b) Weight transient curve of NdCrO₄ kept in H₂ at 380°C. The atmosphere is switched from pure Ar to H₂ at the point indicated by blue dashed line.

Fig. 4 *In situ* FT-IR of (a) NdCrO_4 and (b) CaCrO_4 during reduced at 380°C in H_2 and re-oxidized at 380°C in air after 30 min reduction. In (a) and (b), Red spectra show the reduced and blue ones the reoxidized. Numbers beside the panels show reduction and re-oxidation time. The sharp peak near 3350 cm^{-1} is the noise from detector. In (b), the peak at around 3650 cm^{-1} is assigned to the second overtone of CrO_4^{2-} stretching band.

Fig. 5 Cross-section SEM of NdCrO₄ layer deposited on Si wafer by screen-printing method.

Fig. 6 Fuel cell performances of PCFC with NdCrO_4 interlayer (red) and without the interlayer (black) at 500°C .