



Short communication

Use of layered double hydroxides to improve the triple phase boundary in anion-exchange membrane fuel cells

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ABSTRACT

We propose a novel approach that uses a positively charged inorganic compound, layered double hydroxide (LDH), as an anion conductor in anion-exchange membrane fuel cells to improve the triple phase boundary (TPB) of catalyst layers. Pt/C catalyst layers with hydrothermally prepared Mg–Al- and Ni–Al-based LDHs (MgAl-LDH and NiAl-LDH, respectively) were constructed, and their oxygen-reduction currents were evaluated under the same conditions as in anion-exchange membrane fuel cells. Scanning electron microscopy and a surface-area analysis revealed that the two LDHs had almost the same surface-area, size, and hexagonal cylinder structure. In contrast, electrochemical measurements showed that MgAl-LDH improved the current densities while NiAl-LDH showed the same current densities as the catalyst layer with no LDHs. These results suggest that MgAl-LDH introduced OH⁻-conducting paths within the catalyst layers and effectively increased the TPB region in anion-exchange membrane fuel cells.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are expected to be a next-generation high energy-density power source. PEFCs usually include perfluorinated cation-exchange membranes such as Nafion, and hydrogen-oxidation and oxygen-reduction reactions occur to generate electric power. In these PEFCs, cell reactions mainly occur at triple phase boundary (TPB) regions that are formed by three phases; catalysts, ion conductors, and gaseous reactants. Therefore, the amount and condition of the TPB are very important factors in determining the performance of PEFCs [1]. In proton exchange membrane fuel cells (PEMFCs), which are a type of PEFC, proton-conducting ionomers such as Nafion solution are used to fabricate an appropriate TPB region in catalyst layers [2]. These proton-conducting ionomers drastically increase the performance of PEMFCs.

An anion-exchange membrane fuel cell (AEMFC) is an attractive power-generation system which has the potential to be the next PEFC. In AEMFCs, cell reactions take place under basic conditions, which leads to the faster electrode-kinetics of oxygen-reduction than with acidic conditions [3]. Since Nafion acts as a proton-conducting ionomer in PEMFCs, ion conductors in AEMFCs should be OH⁻ ion conductors. However, such sufficient materials to transport OH⁻ ions effectively are not available at present. In our group's

previous study, plasma polymerization of 4-vinylpyridine was used to prepare a well-formed TPB region for AEMFCs [4]. More convenient methods for introducing anion-conducting paths in catalyst layers should be explored to improve TPB regions in AEMFCs.

In this study, we focused on layered double hydroxides (LDHs), which are well-known hydrotalcite-like inorganic compounds. LDHs have the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2][(A^{n-})_{x/n} \cdot mH_2O]$, where M^{II} is a divalent cation such as Mg²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Mn²⁺, etc., M^{III} is a trivalent cation such as Al³⁺, Ga³⁺, Fe³⁺, Co³⁺, Mn³⁺, Cr³⁺, etc., and Aⁿ⁻ is an n-valent anion such as Cl⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, organics, etc. Substitution of a fraction of the M^{II} by M^{III} results in a net positive charge on the hydroxide basal layers, which is balanced by exchangeable interlayer anions. Over the past few years, LDHs have received increasing attention due to their versatility and usefulness in a wide range of technological applications as catalysts, anion exchangers, acid adsorbents, etc. [5]. However, to the best of our knowledge, there have been no previous reports on the applicability of LDHs as anion conductors in fuel cells.

The present report describes for the first time an effective approach for the use of LDHs to improve TPB regions for oxygen-reduction by introducing OH⁻-conducting paths in catalyst layers.

2. Experimental

2.1. Preparation and characterization of LDHs

Mg(NO₃)₂·6H₂O, Al(NO₃)₃·6H₂O, and hexamethylenetetramine (HMT) (Nacalai Tesque, Inc.) were used to prepare MgAl-LDH [6].

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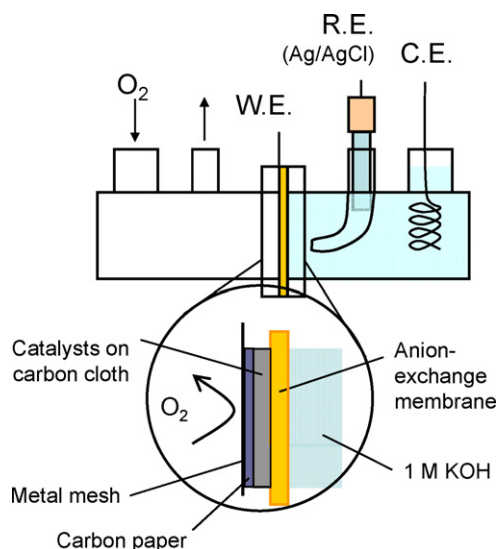


Fig. 1. Schematic illustration of a fabricated half-MEA and an electrochemical cell. Active area: 3.14 cm^2 ; carbon cloth: electrochem EC-CC1-060; carbon paper: SGL carbon GDL10BC.

$\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ were dissolved in de-ionized water in a molar ratio of 2:1 (Mg:Al), and HMT was added to the solution. The resulting mixture was poured into a polytetrafluoroethylene inner vessel within a stainless steel outer vessel. The mixture was allowed to react at 413 K for 24 h under air-tight conditions. The resulting product was filtered with filter paper and repeatedly washed with de-ionized water to remove unreacted residual reagents. After being dried in a vacuum drying oven overnight at 323 K, the obtained powder was sieved (280 mesh). Chemicals such as $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AlCl_3 (anhydrite) (Nacalai Tesque, Inc.), and urea (Sigma–Aldrich Co.) were used to prepare NiAl-LDHs. The precursor molar ratio for NiAl-LDH was 2:1 (Ni:Al). The precursor solution for NiAl-LDH was prepared by a method similar to that for MgAl-LDH, and pyrolyzed at 190 °C for 48 h [7]. The obtained precipitate was characterized by the following techniques: powder X-ray diffraction (XRD), scanning electron microscopy (SEM) observation, Brunauer–Emmett–Teller (BET) surface-area analysis, and Fourier transform infrared (FT-IR) spectroscopy.

2.2. Catalyst layers with LDHs for oxygen-reduction

To evaluate how LDHs affected the TPB region in catalyst layers, half-electrode membrane assemblies (MEAs) were constructed (Fig. 1). Commercially available carbon-supported platinum (Pt/C, E-TEK, 40 wt% Pt) was used as a catalyst, and catalyst inks were prepared by mixing Pt/C, LDHs, water, and glycerol in a weight ratio of 1:0.25:5:20 for 12 h [8]. Catalyst layers were formed by coating a carbon cloth with catalyst inks (by hand-painting) for the given amount of Pt-loading. The amount of Pt-loading was uniformly 1 mg cm^{-2} . Carbon cloths coated with catalyst layers were heated in a vacuum chamber at 408 K for 3 h to remove solvents. These catalyst-coated carbon cloths were pressed onto an anion-exchange membrane (A201, thickness: 28 μm , Tokuyama Corp., Japan) with water-proof carbon paper to construct half-MEAs.

The activities of catalyst layers using LDHs were evaluated in a three-electrode cell with two compartments. One compartment was filled with 1 mol dm^{-3} KOH solution, and a Ag/AgCl electrode (3 mol dm^{-3} KCl) and Pt wire were used as reference and counter electrodes, respectively. The potential of a Ag/AgCl electrode was calibrated by measuring the potential for H_2 oxidation/evolution in 1 mol dm^{-3} KOH solution. The other compartment was supplied with humidified O_2 gas at a flow rate of 50 mL min^{-1} . The half-MEAs

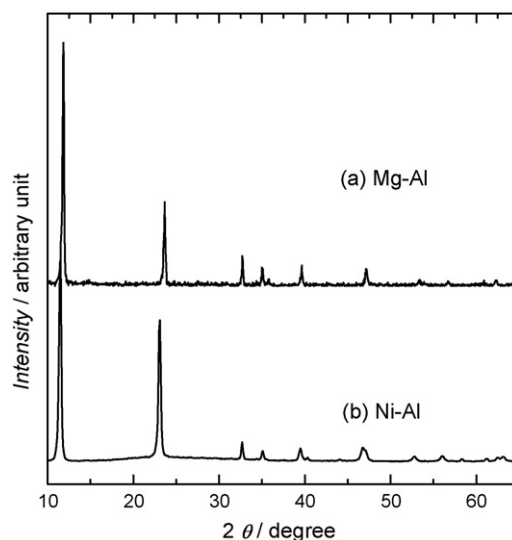


Fig. 2. XRD pattern of the prepared (a) Mg–Al-based and (b) Ni–Al-based products.

prepared as described earlier were placed between these two compartments. With the use of this electrochemical cell, steady-state polarizations were conducted at every 50 mV in a potential range from 1.0 to 0.2 V (vs. RHE). The temperature of the electrochemical cell was set at 303 or 323 K.

3. Results and discussion

3.1. Characterization of LDHs and catalyst layers

The hydrothermally prepared precipitates were white and green materials in $\text{Mg}(\text{NO}_3)_2\text{--Al}(\text{NO}_3)_3\text{--HMT}$ and $\text{NiCl}_2\text{--AlCl}_3\text{--urea}$ systems, respectively. Fig. 2 shows XRD patterns of the two resulting materials. Both XRD patterns showed diffraction of a rhombohedral structure, indicating diffraction patterns at about 12° (003), 23° (006), 32° (009), 35° (012), and 40° (015) [6]. Due to the incorporation of different anion interlayers, the basal spacing of NiAl-LDH (0.77 nm) was greater than that of MgAl-LDH (0.75 nm) in (003) reflection. All XRD patterns of the resultant samples showed single LDH phases and no obvious peaks of by-products, indicating that MgAl- and NiAl-LDHs were successfully prepared.

FT-IR spectra of MgAl- and NiAl-LDH samples are shown in Fig. 3. In the spectrum of MgAl-LDH, the strong peaks at 1356 and 790 cm^{-1} belong to the ν_3 vibration and bending modes of CO_3^{2-} , respectively [9]. Therefore, in the MgAl-system, CO_3^{2-} was the intercalate and Mg–Al– CO_3 LDHs were obtained. The broad band centered at 3440 cm^{-1} is assigned to the O–H stretching modes of interlayer water molecules and H-bonded OH groups. The presence of a shoulder at around 3080 cm^{-1} suggests that water molecules were H-bonded to CO_3^{2-} in the interlayers. The weak band at 1607 cm^{-1} is due to the bending mode of water molecules. Other absorption bands below 800 cm^{-1} are associated with metal–oxygen (M–O) stretching and bending modes. On the other hand, the spectrum of NiAl-LDH was identical to that reported for Cl^- -LDH [9] and had only little peaks that correspond to CO_3^{2-} . Thus, we obtained two different LDHs: MgAl-LDH intercalated with CO_3^{2-} and NiAl-LDH with Cl^- .

Fig. 4(a) and (b) shows SEM images of the MgAl- and NiAl-LDHs. Both the MgAl- and NiAl-LDHs had almost the same hexangular pellet shape with a size of about 3 μm . BET analysis shows that the MgAl- and NiAl-LDHs had almost the same surface areas: 16.0 and $15.1 \text{ m}^2 \text{ g}^{-1}$, respectively. Therefore, we obtained two LDHs with different compositions and a similar size, which could be helpful

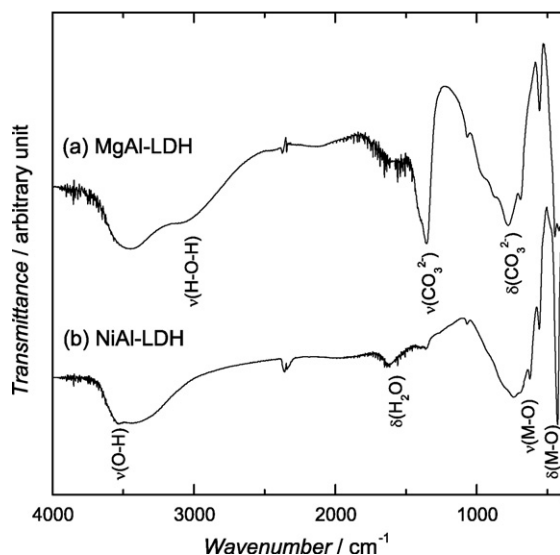


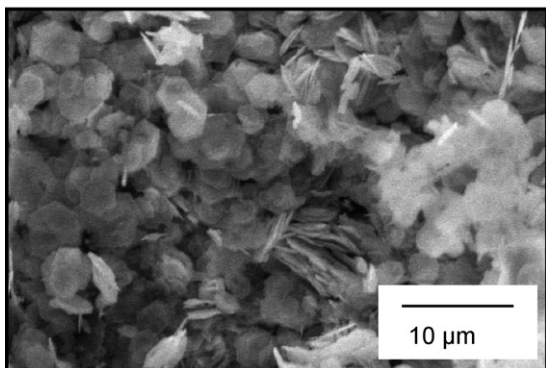
Fig. 3. FT-IR spectra of the prepared (a) MgAl- and (b) NiAl-LDHs.

for evaluating the effect of introducing LDHs in catalyst layers on oxygen-reduction activities.

3.2. Oxygen-reduction activities of catalyst layers with LDHs

Fig. 5 shows the polarization curves of half-MEAs with different catalyst layers (Pt/C only, Pt/C + MgAl-LDH, and Pt/C + NiAl-LDH), which were used to evaluate their oxygen-reduction activities. Each

(a) MgAl-LDH



(b) NiAl-LDH

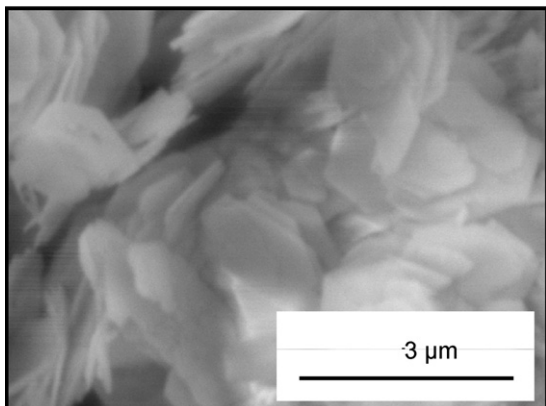


Fig. 4. SEM images of (a) MgAl- and (b) NiAl-LDHs.

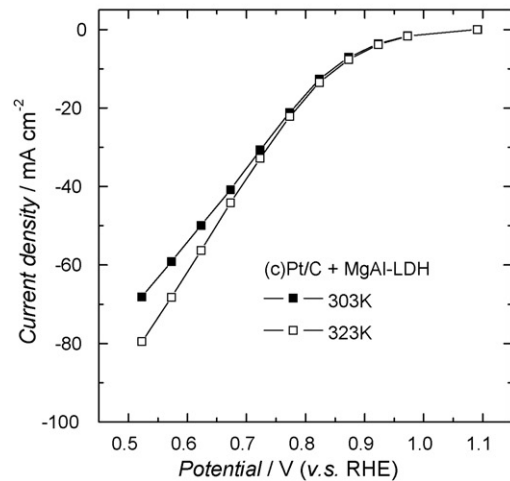
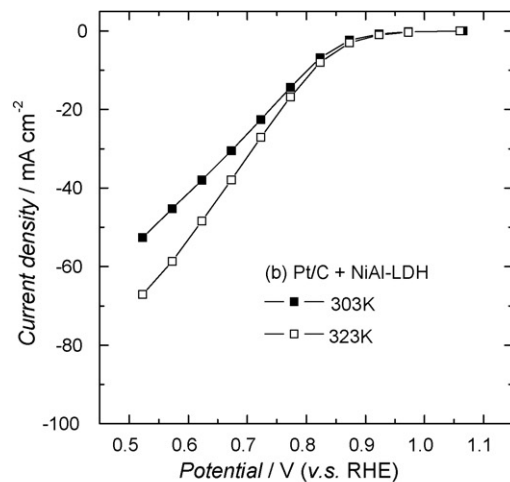
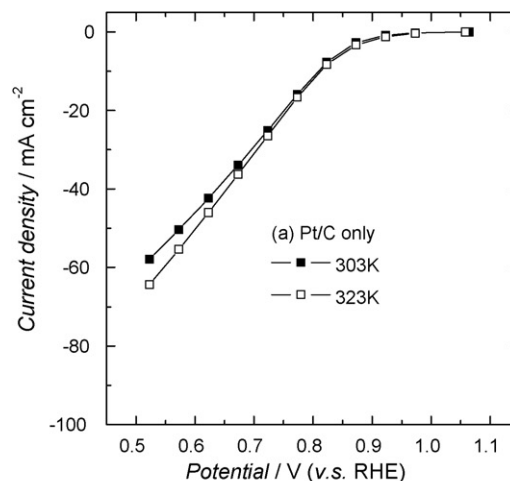


Fig. 5. Steady-state polarization curves of (a) Pt/C only, (b) Pt/C + NiAl-LDH, and (c) Pt/C + MgAl-LDH.

electrode showed almost the same onset potential at 0.95 V (vs. RHE) for oxygen-reduction. This result indicated that the onset potential for oxygen-reduction was an intrinsic characteristic of Pt/C catalysts, and was not affected by the absence or presence of LDHs. In contrast, among the three catalyst layers at 303 K, the catalyst layer consisting of Pt/C + MgAl-LDH showed the largest current densities at all potentials below 0.9 V. In this system, MgAl-LDH had no catalytic activity for oxygen-reduction and no electron conductivity. Therefore, only MgAl-LDH effectively improved the

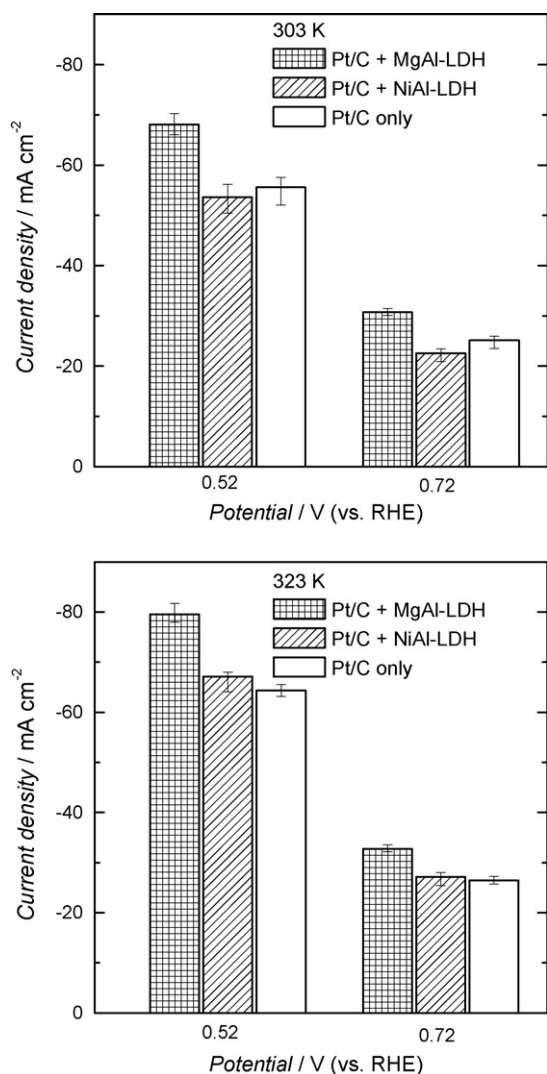


Fig. 6. Oxygen-reduction current densities at 0.52 and 0.72 V (vs. RHE) at (a) 303 K and (b) 323 K. Error bars are obtained from independent repeat experiments.

oxygen-reduction activities of the catalyst layers. As the cell temperature increased to 323 K, the current densities of the three electrodes for oxygen-reduction showed obvious increases, compared with those at 303 K. These increases were mainly due to the catalytic activities of Pt/C for oxygen-reduction [10]. In terms of the Pt mass activity of these three half-MEAs, the performances were lower than those reported in the literature [11]. We believe that the optimization in processing and fabrication of half-MEAs and the pre-treatment of purchased Pt/C catalysts may improve the performance of mass activities.

Fig. 6 shows the results of steady-state polarizations at potentials of 0.52 and 0.72 V (vs. RHE) at 303 and 323 K. The most active half-MEA for oxygen-reduction in this study was Pt/C + MgAl-LDH, and the other two half-MEAs (Pt/C + NiAl-LDH and Pt/C only) showed almost the same current densities at both potentials. We could expect that both MgAl- and NiAl-LDHs would improve the performance of half-MEAs by introducing themselves within catalyst layers. However, NiAl-LDHs did not improve performance in this study. These differences in performance due to LDHs can

be considered from two perspectives. First, LDHs may induce pore formation in the catalyst layers for the smooth supply of oxygen molecules. Second, LDHs may increase the electrochemical active areas (i.e. TPB region) by introducing anion-conducting agents. If we assume that the structure of LDHs determines oxygen-reduction performance, the improvements in performance would be equal, since MgAl- and NiAl-LDHs had almost the same morphologies and structures. However, since MgAl- and NiAl-LDHs had different effects on the performance of half-MEAs, we can reject the first notion.

As mentioned above, LDHs can capture anions such as OH^- , Cl^- and CO_3^{2-} in their interlayers and on their surfaces. Furthermore, the ion conductivities of LDHs vary due to intercalated anions and the composition of the hydroxylated framework [12]. Therefore, it is reasonable to consider that MgAl- and NiAl-LDHs had different anion conductivities and that only MgAl-LDH successfully introduced effective anion-conducting paths within catalyst layers. This resulted in an increase in the TPB region of catalyst layers. Ion conductivities were evaluated by ac impedance measurements conducted under ambient atmospheric conditions. Mixtures of prepared LDHs and polyvinylidene fluoride (90:10 wt%) were pressed to form a pellet (thickness: 1.5–2.0 mm). Such pellet was sandwiched with a two-component cell filled with 1 mol dm^{-3} KOH solution, and two Pt plates were immersed in each component. The real part of the impedance around 1 kHz was used for calculating the ion conductivity. As a result, the ion conductivity of MgAl-LDHs was $9.1 (\pm 0.3) \times 10^{-2} \text{ S cm}^{-1}$, and that of NiAl-LDHs was over the limit of resistance in ac impedance measurements. These differences in ion conductivities were in good agreement with the results of FT-IR analysis. Although ion-conducting inorganic compounds such as LDHs and metal oxides are not as flexible as Nafion ionomers, their chemical and electrochemical stabilities are appealing. We believe that these results will open up new possibilities for the application of LDHs in AEMFCs.

4. Conclusions

Hydrothermally prepared MgAl- and NiAl-LDHs were used with Pt/C to construct cathode catalyst layers in AEMFCs. Electrochemical measurements to evaluate their oxygen-reduction activities revealed that MgAl-LDH improved oxygen-reduction, while NiAl-LDH showed almost the same results as a catalyst layer without LDHs. Therefore, we conclude that MgAl-LDH promoted OH^- transport in catalyst layers, resulting in an increase of the TPB region.

References

- [1] B.C.H. Steele, *J. Mater. Sci.* 36 (2001) 1053–1068.
- [2] E.A. Ticianelli, E.R. Gonzalez, in: W. Vielstich, H.A. Gasteiger, A. Lamm (Eds.), *Handbook of Fuel Cells—Fundamentals, Technology and Applications*, vol. 2, John Wiley & Sons, England, 2003 (chapter 33).
- [3] J.R. Varcoe, R.C.T. Slade, *Fuel Cells* 5 (2005) 187–200.
- [4] K. Matsuoka, S. Chiba, Y. Iriyama, T. Abe, M. Matsuoka, K. Kikuchi, Z. Ogumi, *Thin Solid Films* 516 (2008) 3309–3313.
- [5] S.P. Newman, W. Jones, *New J. Chem.* 22 (1998) 105–115.
- [6] N. Iyi, T. Matsumoto, Y. Kaneko, K. Kitamura, *Chem. Lett.* 33 (2004) 1122–1123.
- [7] L. Li, R. Ma, Y. Ebina, N. Iyi, T. Sasaki, *Chem. Mater.* 17 (2005) 4386–4391.
- [8] M.S. Wilson, S. Gottesfeld, *J. Appl. Electrochem.* 22 (1992) 1–7.
- [9] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* 128 (2006) 4878–4880.
- [10] U.A. Paulus, T.J. Schmidt, H.A. Gasteiger, R.J. Behm, *J. Electroanal. Chem.* 495 (2001) 134–145.
- [11] K.J.J. Mayrhofer, V. Juhart, K. Hartl, M. Hanzlik, M. Arenz, *Angew. Chem. Int. Ed.* 48 (2009) 3529–3531.
- [12] A. Roy, J.P. Besse, *Solid State Ionics* 46 (1991) 95–101.