Water-Insoluble Lanthanum Oxychloride-Based Solid Electrolytes with Ultra-High Chloride Ion Conductivity**

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The chloride ion is well known as one of several migrating anion species in the solid electrolyte field. However, the chloride-ion conductors reported so far are all based on chlorides that are soluble in hot water or water at room temperature. This can be a critical disadvantage for the practical applications of various functional materials. In order to overcome this problem, it is essential to fabricate Cl^- ion-conducting solid electrolytes that are water-insoluble. Since the desired end material is a Cl^- ion-conductor, the solids should contain Cl^- anions. We have previously reported the Ca-doped lanthanum oxychloride solid-solution electrolyte,[1] which has the unique characteristic of being water-insoluble. However, the Cl^- ion conductivity at 700 °C was 2.8×10^{-5} $S\,cm^{-1}$, which is still two orders of magnitude lower than conventional Cl^--ion conductors such as $PbCl_2$,[2] $BaCl_2$,[3] $SrCl_2$,[4] and $CsPbCl_3$.[5]

This report centers on how the properties of this promising material were improved through a ball milling process. Ball milling resulted in a fine, homogeneous mixture of the starting materials, namely LaOCl and $CaCO_3$, which in turn enabled the fabrication of high-density pellets.

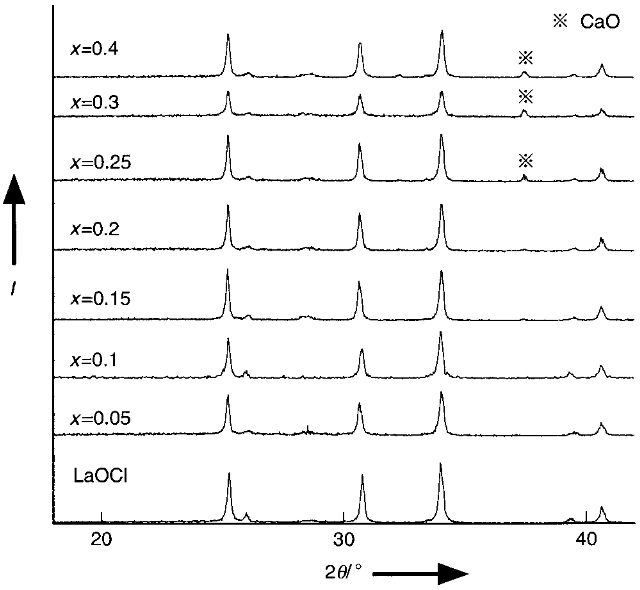

Figure 1. X-ray powder diffraction results for $La_{1-x}Ca_xOCl_{1-x}$ ($x = 0.05$–0.4) solid solutions, along with the data for pure LaOCl.

Figure 1 shows the powder X-ray diffraction (XRD) results for $La_{1-x}Ca_xOCl_{1-x}$ ($x = 0.05$–0.4) solid solutions, along with the data for pure LaOCl. It is expected that LaOCl would form a solid solution with $CaCO_3$ with up to 20 mol% $CaCO_3$. Since the radii of La^{3+} ions and Ca^{2+} ions are so similar (0.130[6] and 0.126 nm,[6] respectively), it is not possible to verify the formation of the solid solution based on changes of lattice parameter. A mixed phase consisting of Ca-doped LaOCl solid solution and CaO was obtained by mixing in $CaCO_3$ at a proportion of above 20 mol%. This clearly indicates that the solubility limit of Ca in LaOCl is around 20 mol%.

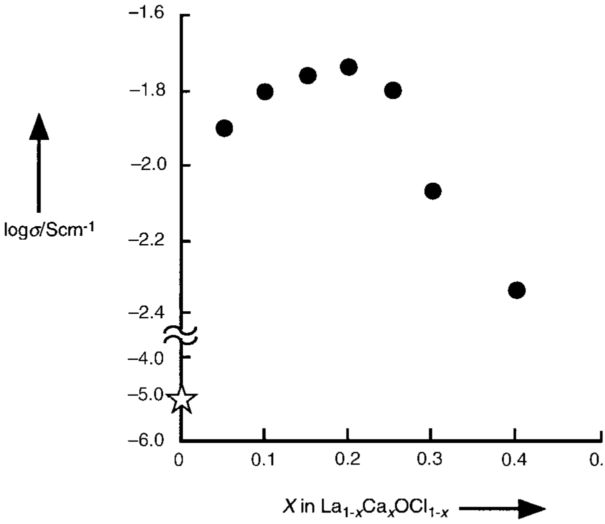

Figure 2. Electrical conductivity at 800 °C as a function of x in $La_{1-x}Ca_xOCl_{1-x}$. The conductivity of pure LaOCl is also plotted (★).

Figure 2 presents the electrical conductivity of $La_{1-x}Ca_xOCl_{1-x}$ at 800 °C as a function of x. At a dopant level of 5 mol% Ca, a sharp enhancement in conductivity of over three orders of magnitude is observed. The Cl^- vacancies formed by substitution of La^{3+} ions by Ca^{2+} ions greatly facilitates Cl^- anion conduction in the LaOCl framework. The conductivity gradually increases with increasing Ca content in the $La_{1-x}Ca_xOCl_{1-x}$ solid solution, with the highest (1.9×10^{-2} $S\,cm^{-1}$) observed for $La_{0.8}Ca_{0.2}OCl_{0.8}$, which corresponds to $x = 0.2$. A further increase of the Ca content results in a rapid decrease in conductivity, which results from the formation of the secondary CaO phase. These results corroborate that LaOCl forms a $La_{1-x}Ca_xOCl_{1-x}$ solid solution with up to 20 mol% Ca doping.

Figure 3 displays the conductivity of $La_{0.8}Ca_{0.2}OCl_{0.8}$, which exhibits the highest Cl^- ion conductivity in the $La_{1-x}Ca_xOCl_{1-x}$ series, as a function of temperature. This is presented with data for pure LaOCl, the previously reported 1.6 mol% Ca-doped LaOCl solid solution,[1] and two typical Cl^- conductors, namely $PbCl_2$ and $CsPbCl_3$, which both exhibit a reasonably high Cl^- ion conductivity. The conductivity of the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution, with an activation

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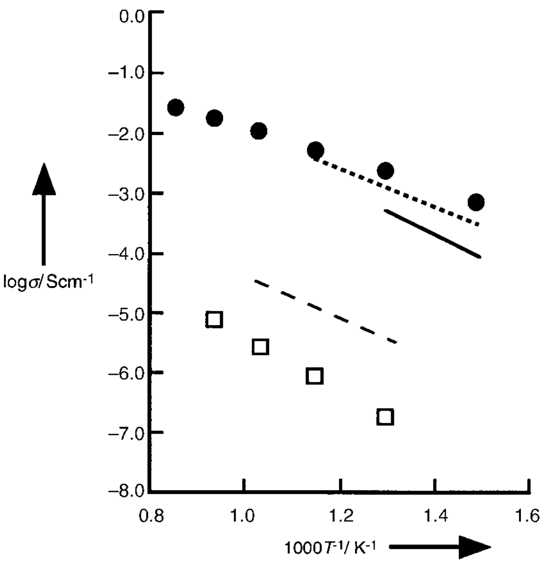

Figure 3. A plot of the conductivity of the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution (●) as a function of temperature. Also shown are the data for pure LaOCl (□), the $La_{0.984}Ca_{0.016}OCl_{0.984}$ solid solution (– – –),[1] and the conventional Cl^- ion conductors $PbCl_2$ (——) and $CsPbCl_3$ (- - - -)[5] which exhibit a high Cl^- ion conductivity.

energy of 51.5 kJ mol^{-1}, is more than two orders of magnitude higher than that of the 1.6 mol% Ca-doped LaOCl solid solution. The conductivity of the former also exceeds that of conventional Cl^- ion conductors. Unlike chlorides, such as $PbCl_2$ and $CsPbCl_3$, which are all soluble in hot water and cannot be used for high-temperature applications because of their low melting points (501 and 604 °C for $PbCl_2$ and $CsPbCl_3$, respectively[5]) and their low stability in water vapor-containing environments, the present $La_{1-x}Ca_xOCl_{1-x}$ solid solutions are insoluble in water, and are thermally stable at temperatures as high as 1000 °C. These unique characteristics enable the application of these solid electrolytes as functional devices under a variety of atmospheric and thermal conditions.

To identify the conducting species in $La_{0.8}Ca_{0.2}OCl_{0.8}$, polarization measurements were carried out at 700 °C in oxygen (10^5 Pa), helium (4 Pa), and 1 vol% chlorine (in nitrogen) atmospheres. The results are shown in Figure 4; σ_{dc} and σ_{ac} denote the DC and AC conductivity, respectively. In both oxygen and helium atmospheres, a considerably high degree of polarization was observed, while no polarization was observed in 1 vol% chlorine at all. This indicates that Cl^- anions formed from the chlorine atmosphere at the cathode migrate through the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution and reach the anodic surface to be released as chlorine gas. The results suggest that the predominant migrating species is the Cl^- anion. Based on the polarization behavior in oxygen and helium, the Cl^- anion transference number was estimated to be higher than 0.98.

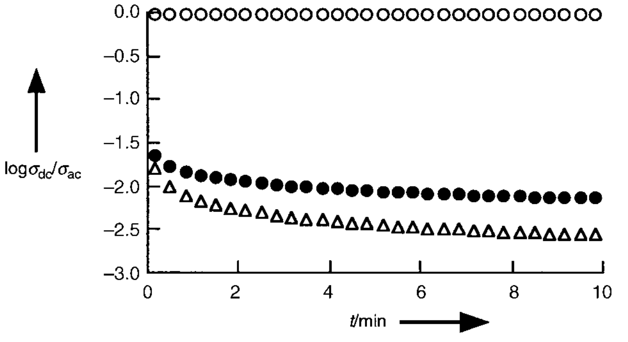

Figure 4. Polarization measurements for the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution in O_2 (●), He (△), and 1 vol% Cl_2 in N_2 (○) at 700 °C.

Table 1 displays the relative density and Vickers hardness of the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution, as well as the data for pure LaOCl, $La_{0.984}Ca_{0.016}OCl_{0.984}$,[1] and $La_{0.8}Ca_{0.2}OCl_{0.8}$ processed without ball milling. As a consequence of the ball milling step utilized in the present study, the relative density was increased to 95.9 %, compared with 92.9, 91.3, and 93.3 % for pure LaOCl, $La_{0.984}Ca_{0.016}OCl_{0.984}$, and the unmilled $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution, respectively. Consequently, the Vickers hardness of the ball-milled material was 115, compared with 33, 42, and 30 for the other materials. The improved relative density and mechanical strength would be a distinct advantage for practical applications.

Table 1. The relative density and the Vickers hardness of the $La_{0.8}Ca_{0.2}OCl_{0.8}$ solid solution, compared with the data for pure LaOCl, $La_{0.984}Ca_{0.016}OCl_{0.984}$,[1] and unmilled $La_{0.8}Ca_{0.2}OCl_{0.8}$.

Solid electrolyte	Relative density [%]	Vickers hardness
$La_{0.8}Ca_{0.2}OCl_{0.8}$ (ball milled)	95.9	115
pure LaOCl	92.9	33
$La_{0.984}Ca_{0.016}OCl_{0.984}$	91.3	42
$La_{0.8}Ca_{0.2}OCl_{0.8}$ (unmilled)	93.3	30

In conclusion, a wide range of Ca-doped LaOCl solid solutions were prepared by ball milling, which enhanced the Cl^- ion conductivity by more than three orders of magnitude in comparison with that of pure LaOCl. The Ca-doped LaOCl solid-solution electrolyte has the unique feature of being insoluble in water, in addition to possessing a higher relative density and hardness, while being thermally stable at temperatures as high as 1000 °C. This novel Cl^- ion conducting solid series is expected to enable the fabrication of an array of new functional materials.

Experimental Section

La_2O_3 was dissolved in hydrochloric acid (3 N). LaOCl was prepared by evaporating away the water from this solution and heating in air at 700 °C for 12 h. The appropriate amount of LaOCl and $CaCO_3$ was ball milled (Fritsch Pulverisette 7) for 12 h. The pulverized mixture was pelletized and heated at 1000 °C for 12 h to form the $La_{1-x}Ca_xOCl_{1-x}$ solid solution. The RuO_2 pellet that served as the electrode was obtained by heating pelletized RuO_2 at 700 °C for 6 h in air.

The formation of the solid solution electrolyte was confirmed by powder XRD analysis (M18XHF, Mac Science). The data were collected by a step-scanning method in the 2θ range of 10–70° with a step width of 0.02° using $Cu_{K\alpha}$ radiation. The Ca ratio in the solid-solution electrolyte was determined by inductively coupled plasma (ICP) analysis (Shimadzu ICPS-1000IV). The AC conductivity measurements were carried out using two platinum electrodes as ion-blocking electrodes by a complex impedance method in the frequency range from 5 Hz to 13 MHz (Precision LCR meter 4192A, Hewlett Packard) between 400 °C and 900 °C in air. AC conductivity was found to be independent of the atmosphere used during the measurements. The polarization measurements were conducted by applying a constant current (1 μA) between the two RuO_2 electrodes. The voltage was measured as a function of time at 700 °C. RuO_2 electrodes were utilized when the atmosphere contained Cl_2 because this would react with Pt electrodes. DC conductivity determination was based on the voltage, applied current, RuO_2 electrode surface area, and pellet thickness. Details of similar experiments are described elsewhere.[7]

The relative density and the Vickers hardness of the pellets were measured by a Micromeritics (AccuPyc 1330) porosimeter and a Shimadzu Micro Hardness Tester (HMV-2).

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[1] N. Imanaka, K. Okamoto, G. Adachi, *Chem. Lett.* **2001**, 130.

[2] K. J. De Vries, J. H. Van Stanten, *Physica* **1963**, *29*, 482.

[3] C. E. Derrington, M. O'Keeffe, *Solid State Commun.* **1974**, *15*, 1175.

[4] G. M. Hood, J. A. Morrison, *J. Appl. Phys.* **1967**, *38*, 4796.

[5] J. Mizusaka, K. Arai, K. Fueki, *Solid State Ionics* **1983**, *11*, 203.

[6] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751.

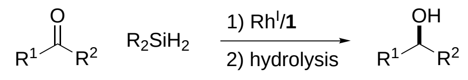
[7] Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, G. Adachi, *Chem. Mater.* **1997**, *9*, 1649.

Application of a New Family of P,N Ligands to the Highly Enantioselective Hydrosilylation of Aryl Alkyl and Dialkyl Ketones**

Beata Tao and Gregory C. Fu*

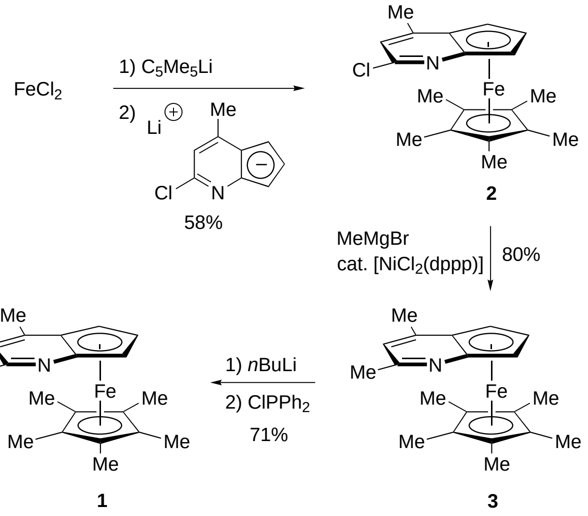
Due in large part to the utility of enantiomerically enriched alcohols and their selectively O-protected derivatives, considerable energy has been devoted to the search for efficient catalysts for the asymmetric hydrosilylation of ketones.[1] Very good enantioselectivities have been obtained for many aryl alkyl ketones, but for dialkyl ketones they are generally more modest. Seminal discoveries have resulted from these efforts, including the development of pybox, the first highly effective bis(oxazoline)-based ligand.[2,3]

During the past few years, we have been pursuing the design and development of new chiral ligands that are based on “planar-chiral” heterocycles,[4] and for several metal-catalyzed processes we have demonstrated that this family of ligands can provide enantioselectivity superior to the best methods that had previously been reported.[5] Here we describe the synthesis of a new planar-chiral P,N ligand, and we establish its exceptional efficiency in rhodium-catalyzed asymmetric hydrosilylations of aryl alkyl ketones and dialkyl ketones [Eq. (1)].



(1)

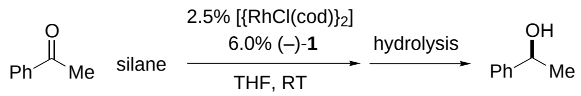
The synthesis of planar-chiral ligand **1** is illustrated in Scheme 1.[6] Treatment of $FeCl_2$ with C_5Me_5Li and then 2-chloro-4-methyl-7*H*-cyclopenta[b]pyridinyllithium affords ferrocene derivative **2**.[7] Kumada coupling of **2** with MeMgBr furnishes **3**, which is lithiated and then quenched with $ClPPh_2$ to provide ligand **1**, the enantiomers of which are readily resolved by chiral HPLC. We have determined the absolute configuration of (−)-**1** by X-ray crystallography.



Scheme 1. Synthesis of planar-chiral P,N ligand **1** (only (+)-**1** is depicted). dppp = 1,3-bis(diphenylphosphanyl)propane.

For an initial investigation of the utility of ligand **1**, we chose to focus on the rhodium-catalyzed asymmetric hydrosilylation of ketones. Specifically, we examined the reduction of acetophenone, and we discovered that the level of enantioselectivity is highly dependent on the choice of silane (Table 1). Thus, monoalkyl- and monoaryl silanes (entries 1 and 2), as well as dialkyl silanes (entry 3), furnish disappoint-

Table 1. Hydrosilylation of acetophenone catalyzed by Rh^I/(−)-**1**: enantioselectivity as a function of the silane.



Entry	Silane	*ee* [%][a]
1	*n*-octylSiH_3	3
2	$PhSiH_3$	8
3	Et_2SiH_2	1
4	$PhMeSiH_2$	66
5	Ph_2SiH_2	80
6	*o*-Tol$PhSiH_2$[b]	95
7	*o*-Tol_2SiH_2[b]	92
8	$MesPhSiH_2$[c]	98
9	Mes_2SiH_2[c]	(no reaction)

[a] Average of two runs. [b] Tol = tolyl. [c] Mes = Mesityl.

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