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Reactivity and stability of rare earth oxide–Li_2CO_3 mixtures

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Abstract

The thermal stability of a mixture of Li_2CO_3 and rare earth oxide (R_2O_3) was examined under a dry condition. The heat-treatment of the mixture in CO_2 ambience resulted in the formation of rare earth carbonates for R = La, Pr, Nd, Sm, Eu, and Gd except for Ho–Lu and Y. Lithiation of their rare earth dioxymonocarbonate, i.e., $R_2O_{2+2x}(CO_3)_{1-x}Li_{2x}$ was confirmed for R = La, Pr, Nd, and Sm when the mixture was heated at 900 °C. The lithiation degree, x, was increased with an increase in the heat-treatment temperature in CO_2 and was lower than 0.3. The stability of lithium rare earth dioxymonocarbonate decreased with the atomic number of the rare earth. The high reactivity of the light rare earth oxides with Li_2CO_3 would be attributed to that the large R^{3+}–O^{2-} distance for CN = 5 and 6 with an increase in the ionic $[R^{3+}]/[O^{2-}]$ ratio for the rare earth oxides and is very similar with that of the rare earth dioxymonocarbonates.

Keywords: Powders-solid state reaction; Powders-gas phase reaction; X-ray methods; Sensors; Rare earth dioxymonocarbonate; Li_2CO_3

1. Introduction

The increasing need for reliable and continuous monitoring of CO_2 levels in the atmosphere has promoted the development of potentiometric sensors using a cation conducting solid electrolyte and an auxiliary phase on the measuring electrode.[1–5] A potentiometric CO_2 sensor with a Li_2CO_3 layer as an auxiliary electrode shows satisfactory performances with a fast response, appreciable sensitivity and gas selectivity. However, the sensors show a lack of reproducibility and long-term stability.[6–11] To improve the long-term stability, a new auxiliary electrode material based on Li_2CO_3 and Nd_2O_3 was developed.[12,13] We also confirmed similar additive effects on the sensing performance for several rare earth oxides. When only Li_2CO_3 was used as an auxiliary electrode in a lower level of CO_2, the concentration of Li_2O in the layer increased, and the formed oxide reacted with a solid electrolyte such as a NASICON. For a mixture of Li_2CO_3 and rare earth oxide, the formation of rare earth carbonate and oxycarbonate is expected. The rare earth carbonates and their decomposition and synthesis had been the subject of many investigations. The thermal decomposition of anhydrous rare earth carbonate to oxide occurs *via* intermediate oxycarbonate phases. The stoichiometric rare earth oxycarbonates are monoxydicarbonate, $R_2O(CO_3)_2$, and dioxymonocarbonate, $R_2O_2CO_3$. Attfield and Ferey reported that the lithium-containing lanthanum dioxycarbonate type phase ($La_2O_{2+2x}(CO_3)_{1-x}Li_{2x}$, $x = 0.26$) was formed when a mixture of La_2O_3 and Li_2CO_3 was heated at 550 °C in air.[14] In our previous studies, we investigated the formation of a lithiated rare earth dioxycarbonate, $Nd_2O_{2+2x}(CO_3)_{1-x}Li_{2x}$ using a mixture of Nd_2O_3 and Li_2CO_3 in CO_2.[15] In this case, pure Nd_2O_3 did not react with CO_2 gas to form the $Nd_2O_2CO_3$ at all. However, the $La_2O_2CO_3$ was easily formed by the reaction of a pure La_2O_3 with CO_2.[16]

In this work, the reactivity of Li_2CO_3 with a variety of rare earth oxides and the heat treatment of the mixture in CO_2 were examined to develop new auxiliary electrode materials for a potentiometric CO_2 gas sensor. Especially, the thermal stability of the mixtures and thermal products were examined.

2. Experimental

Commercially available rare earth oxalates of $La_2(C_2O_4)_3{\cdot}9H_2O$ and $Ln_2(C_2O_4)_3{\cdot}10H_2O$ (Ln = Nd, Gd, Dy, and Ho) (99.9%), rare earth oxides (99.9%) and Li_2CO_3 (99.9%) were

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used as starting materials. The rare earth oxides powders were pre-heated at 400 °C in air before the mixing. Mixtures of an oxide and Li_2CO_3 at a 1:1 molar ratio were pulverized and mixed under dry condition by ball milling in a Nylon pot and with Y-stabilized zirconia balls. Thermal studies were carried out with thermogravimetric analysis (TGA) and differential thermal analysis (DTA) under synthesized air (syn-air, <0.5 ppm CO_2) and 100% CO_2 for the mixtures at a heating and cooling rate of 5 °C/min. The crystal structure and the components of the mixtures were examined by the powder XRD method (Cu Kα).

3. Results

3.1. *Formation of carbonates*

For the mixtures of R_2O_3 and Li_2CO_3, the formations of some compounds such as $R_2(CO_3)_3$, $R_2O(CO_3)_2$, $R_2O_2CO_3$, and $LiR(CO_3)_2$ are expected by the heat treatment in CO_2. The rare earth ions should react in ground water with a 100–200 ppm carbonate ion concentration to form $[RCO_3]^+$ and $[R(CO_3)_2]^-$ complexes, although $R_2(CO_3)_3$ is the most stable solid carbonate phase under these conditions. The water molecules of rare earth carbonate hydrate are released in a single stage somewhere between 150 and 300 °C. Furthermore, the thermal decomposition of anhydrous rare earth carbonate to oxide occurs via intermediate oxycarbonate phases. The stoichiometric oxycarbonates are monooxydicarbonate, $R_2O(CO_3)_2$, and dioxymonocarbonate, $R_2O_2CO_3$. The decomposition of anhydrous rare earth carbonates begins above 350 °C. In air and CO_2 atmosphere, the formation of $R_2O(CO_3)_2$ has been reported for the lighter lanthanides.[17,18] The stability of the oxycarbonate phase in air decreased with the increasing atomic number of the rare earth.[19] $Nd_2O_2CO_3$, for example, is stable in air to 750 °C and $La_2O_2CO_3$ is stable in CO to nearly 1000 °C.[20] Solid state rare earth carbonates can be prepared by the following two precipitation methods: (1) by adding alkali or ammonium carbonate or hydrogen carbonate to a solution of the metal salt and (2) by passing carbon dioxide through an aqueous suspension of the metal hydroxide. The ternary carbonates $LiR(CO_3)_2$ with R = La to Lu and Y were synthesized from mixtures of lithium carbonate and $R_2(C_2O_4)_3{\cdot}xH_2O$ under 2000 atom CO_2 and 500 °C.[21]

For rare earth oxides heated in CO_2, the following reactions are expected:

$$R_2O_3 + 3CO_2 \rightarrow R_2(CO_3)_3 \tag{1}$$

$$R_2O_3 + 2CO_2 \rightarrow R_2O(CO_3)_2 \tag{2}$$

$$R_2O_3 + CO_2 \rightarrow R_2O_2CO_3 \tag{3}$$

$$R_2O_3 + xCO_2 \rightarrow R_2O_{2+x}(CO_3)_{1-x} \text{ or } R_2O_3{\cdot}xCO_2 \tag{4}$$

In the case of hydrous rare earth oxalates decomposed by heat treatments in air, the decomposition steps are described as

$$\begin{aligned} &R_2(C_2O_4)_3{\cdot}nH_2O \rightarrow R_2(C_2O_4)_3 \\ &\rightarrow R_2(C_2O_4)(CO_3)_2 \rightarrow R_2(CO_3)_3 \rightarrow R_2O(CO_3)_2 \\ &\rightarrow R_2O_2CO_3 \rightarrow R_2O_3 \end{aligned} \tag{5}$$

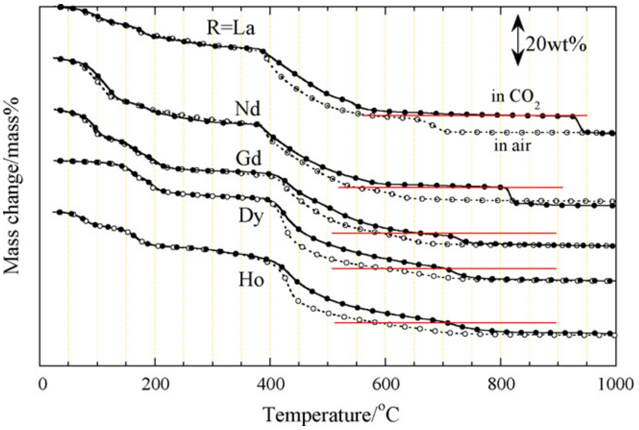

Fig. 1. TGA results for rare earth oxalates $R_2O_2CO_3{\cdot}nH_2O$ (R = La, Nd, Gd, Dy, and Ho) in air (○) and in CO_2 (●).

Fig. 1 shows the TGA results in syn-air and CO_2 for some oxalates. In the thermal decomposition of the hydrous oxalates at a constant heating rate, the anhydrous carbonate, $R_2(C_2O_4)_3$ was formed at around 380 °C and then the weight decreased in air and CO_2. For La-oxalate, the weight decreased in two steps and decomposed to La_2O_3 at 690 and 940 °C in air and CO_2, respectively. The weight estimations suggested the formation of $R_2O_2CO_3$ for R = La–Gd, and its decomposition temperature to R_2O_3 is 940, 815 and 730 °C for La, Nd and Gd in CO_2, respectively. The formation of the $R_2O_2CO_3$ single phase for R = La and Nd by the heat treatment of the rare earth oxalates in CO_2 was confirmed using XRD. The results and the estimated lattice parameters were fairly agreed with the published information in ICSD files (No. 202988: $La_2O_2CO_3$, hexagonal, *P*63/*mmc*, No. 6297: $Nd_2O_2CO_3$, hexagonal, *P*63/*mmc*). In air, the formed $R_2O_2CO_3$ decomposed to R_2O_3 at 700 and 630 °C for La and Nd, respectively. In addition, any plateau region could not be observed for the heavier rare earth oxalates of R = Gd, Dy, and Ho. It was concluded that the stability of $R_2O_2CO_3$ decreased in air and CO_2 ambient with the atomic number of the rare earth (R = La, Nd, Gd, Dy and Ho).

3.2. *Heat-treated products of the mixture*

To clarify the effects of the ambient on the thermal stability of the 1:1 mixtures of lithium carbonate and rare earth oxides, thermal studies were carried out under syn-air and CO_2 ambient at a constant heating rate of 5 °C/min. The TGA results of the mixtures in syn-air and CO_2 are shown in Figs. 2 and 3 for the light (La–Gd) and heavy (Dy–Lu) rare earths with Y, respectively. For the La_2O_3 system in CO_2, the weight increased gradually to 700 °C with temperature. A further heating resulted in a gradual decrease and a following a steep decrease at 960 °C. It should be noted that the weight observed at 980 °C is comparable to that of the starting mixture. In the heating process, the melting of Li_2CO_3 was detected at 716 °C by DTA, which is comparable to that of only Li_2CO_3. This observed coincidence suggests that Li_2CO_3 is stable in CO_2 even in the melted phase. An increase and a following decrease in the weight was confirmed also for the mixture for R = Pr, Nd, Sm, Eu and Gd. For CeO_2 and R_2O_3