Garnet-like solid state electrolyte Li$_6$BaLa$_2$Ta$_2$O$_{12}$ based potentiometric CO$_2$ gas sensor

Yongming Zhu$^{a,c,*}$, Venkataraman Thangadurai$^b$, Werner Weppner$^c$

$^a$ Faculty of Applied Chemistry, Harbin Institute of Technology (Weihai), 264209 Weihai, China
$^b$ Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4, Canada
$^c$ Institute of Inorganic Chemistry, Christian-Albrechts University, Max-Eyth-Str. 2, D-24118, Kiel, Germany

**A R T I C L E   I N F O**

Article history:
Received 25 June 2012
Received in revised form 10 September 2012
Accepted 10 October 2012
Available online xxx

**Keywords:**
Garnet-like
Li$_6$BaLa$_2$Ta$_2$O$_{12}$
Li$_{0.36}$WO$_3$
CO$_2$
Gas sensor

**A B S T R A C T**

A new electrochemical cell for CO$_2$ sensing has been set up using garnet-like solid electrolyte Li$_6$BaLa$_2$Ta$_2$O$_{12}$ and Li$_{0.36}$WO$_3$ as a reference electrode. The electromotive force (EMF) of the cell, the reproducibility and the long-term stability of the sensor signals have been examined at temperatures between 300 and 500 °C. The EMF was found to be dependent on the partial pressure of CO$_2$ (pCO$_2$) and could be expressed by the Nernst equation. The sensitivity of the sensors was 73 mV/decade and 75 mV/decade at 450 and 500 °C, respectively. It was also seen that the sensor showed fast response for CO$_2$ and the sensor signals was found to be highly reproducible and stable for several days.

© 2012 Elsevier B.V. All rights reserved.

**1. Introduction**

There have been increasing needs for all-solid-state CO$_2$ sensors which are highly reliable, inexpensive and compact, from the recent deepening concern about the emissions of greenhouse gases as well as from the growing needs of CO$_2$ monitoring in various fields. Potentiometric devices combining a solid electrolyte with an auxiliary phase of carbonate are eminently suited for practical applications [1]. Lithium electrolyte based CO$_2$ sensors are known to be promising due to their fast response than any other alkali ion conducting materials [2,3]. However, they have some problems such as poor long-term stability [4]. There is still much need for developing new CO$_2$ sensing materials for low operating temperatures. Recently, the Li-stuffed garnet-related structure Li$_5$L$_4$Ta$_2$O$_{12}$ (A = Nb, Ta) have been found as a new class of fast Li-ion conductors with high bulk ionic conductivity, $\sigma_b$, of about $10^{-6}$ s$^{-1}$ at 25 °C [5]. Among the various known garnets Li ion conductors, Ba-doped, Li$_6$BaLa$_2$Ta$_2$O$_{12}$ exhibits total (bulk + grain-boundary) conductivity $\sigma_{total}$ = $4 \times 10^{-5}$ S cm$^{-1}$ at 22 °C with an activation energy of 0.40 eV [6–10].

In the present work, a novel solid state potentiometric CO$_2$ sensor was fabricated using the garnet-like fast lithium ion conductor Li$_6$BaLa$_2$Ta$_2$O$_{12}$ as the solid electrolyte. Li$_2$CO$_3$ and Au paste were employed as the sensing electrode [4,11]. Lithium tungsten oxide of the nominal chemical composition Li$_{0.36}$WO$_3$ was used as the reference electrode.

**2. Experimental**

2.1. Fabrication of sensor devices

Compound with the chemical formula Li$_6$BaLa$_2$Ta$_2$O$_{12}$ was prepared according to the solid state reaction process [5]:

$$3\text{Li}_2\text{CO}_3 + \text{BaCO}_3 + \text{La}_2\text{O}_3 + \text{Ta}_2\text{O}_5 \rightarrow \text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12} + 4\text{CO}_2$$

(1)

using appropriate amounts of high purity (>99.9%) La$_2$O$_3$ (pre-dried at 900 °C for 24 h), Li$_2$CO$_3$, BaCO$_3$, and Ta$_2$O$_5$ obtained from Fluka or Aldrich. 10 wt.% excess of Li$_2$CO$_3$ was added to compensate loss due to volatilization of Li$_2$O during the preparation. The mixtures were heated in air and maintained at 700 °C for 6 h and then annealed at 900 °C for 24 h. Before and after the first step, the powders were ball-milled using zirconium balls for about 12 h in 2-propanol. For the second step of heat treatment, the reaction products were pressed into pellets by isostatic pressure and covered with powder of the same mother composition to reduce the loss of lithium because of volatilization. Afterward, the raw...
material was cut into a shape of disk 8 mm in diameter and 1 mm thickness.

Oxides of the nominal chemical composition Li$_{0.36}$WO$_3$ was prepared according to the solid state reaction process [12].

$$\frac{x}{2} \text{Li}_2\text{WO}_4 + \frac{3 - 2x}{3} \text{WO}_3 + \frac{x}{6} \text{W} \rightarrow \text{Li}_x\text{WO}_3$$  \hspace{1cm} (2)

Appropriate amounts of Li$_2$WO$_4$ (Strem, 98%), WO$_3$ (Alfa, 99.99+%) and W (Alfa, 99.9%) were ball milling for 12 h used zirconium balls with 2-propanol, then dried in air overnight. The sintered step should finish in Ar gas at temperature of 750 °C for 2 h with heating and cooling rates of 1 °C/min. After that, the powder was isostatically pressed at 120 kN for 20 min, then calcined at 750 °C for 2 h in Ar. It was also cut into the shape of a disk of 8 mm in diameter and 1 mm in thickness typically.

The prepared solid electrolyte and Li$_{0.36}$WO$_3$ were pressed together, and the assembly was sealed on the side surface with high temperature ceramic adhesive (940 Cotronics Corp., N.Y.). Li$_2$CO$_3$ (Merck, 99%) and nano Au particles (Product No. C5755A, Heraeus Inc.) (Li$_2$CO$_3$:Au = 3:2 in wt.%) were screen-printed on the top side of the electrolyte, on the reference side nano Au particles were screen-printed on. Two Au wires were attached on both sides, then the assembly was heat treated at 600 °C for 2 h to remove the organic components. After that, ceramic adhesive was used to seal reference electrode Li$_{0.36}$WO$_3$. The schematic structure is shown in Fig. 1.

The phase formation of the investigated samples was characterized through powder X-ray diffractometer (Seifert, XRD 3000TT, using Cu $K_{\alpha}$ radiation at wavelength $\lambda = 0.1541$ nm). The electrical conductivity was measured by AC impedance method using a frequency impedance analyzer (Hewlett-Packard, model 4192A) in the frequency range of 5 Hz–13 MHz at 25–500 °C.

### 2.2. Evaluation of sensing properties

Sensor characteristics were measured using a testing chamber (Kiel Cell KC 2.0, Ionic Systems Inc.), consisting of a ceramic sensor-mounting inside a quartz-glass tube (with diameter of inside glass tube 35 mm and length of glass tube 350 mm) placed into a split tube laboratory furnace (TF 2.0, Ionic Systems Inc.), provided with a gas inlet and outlet. The sensors were heated externally through the furnace during measurement. The EMF was recorded in different CO$_2$ concentrations ranging from 1000 ppm (0.1%) up to 100,000 ppm (10%), using a Keithley 2000 digital multimeter (Keithley Instruments Inc., USA) with an input resistance of >10 GΩ and adapted data collection software. CO$_2$ concentrations were adjusted using different mass flow controllers (Tylan 2900 Series) varying the flows of dry synthetic air (21 vol.% O$_2$ in N$_2$), 1% CO$_2$ (1 vol.% CO$_2$ in synthetic air) and 10% CO$_2$ (10 vol.% CO$_2$ in synthetic air) through the quartz tube while keeping the overall flow rate constant at 70 ml/min. The sample holder needs 14.1 min to get a new CO$_2$ gas concentration under this flow rate.

### 3. Results and discussion

#### 3.1. Characterization of electrolyte and auxiliary layer

Garnets are orthosilicates with the general structural formula, A$_n$B$_{12}$O$_{32}$Si$_4$O$_{12}$, where A and B refer to eight-coordinated and six-coordinated cation sites [13], respectively. SiO$_4$ tetrahedral is isolated and connected to each other through ionic bonds with the interstitial B-cations. A large variety of complex oxides have also been found to crystallize in garnet-like structures with other elements replacing silicon, for example, A$_n$B$_{12}$O$_{32}$ (A = Ca, Mg, Y, La or rare earth; B = Al, Fe, Ga, Ge, Mn, Ni, V). The powder XRD pattern for Li$_6$BaLa$_2$Ta$_2$O$_{12}$ was calculated using the atomic positions from single crystal data employing software Powder Cell program. As expected, the cubic lattice constant for Li$_6$BaLa$_2$Ta$_2$O$_{12}$ is 12.948(2) Å, the 8-fold coordination ionic radius for Ba$^{2+}$ is 1.44 Å. According to JCPDS data (No. 76-1497), Li$_{0.36}$WO$_3$ retains its crystallographic phase (cubic) and there is no new phase in the as prepared cubic structure (Fig. 3). The Arrhenius plot for the total (bulk + grain-boundary) electrical conductivity of Li$_6$BaLa$_2$Ta$_2$O$_{12}$ was shown in Fig. 4. The data obtained from heating and cooling cycle follow the same line with activation energy of 0.40 eV for Li$_6$BaLa$_2$Ta$_2$O$_{12}$, which is comparable to those values previously reported for the lithium ion conductor LISICON (0.56 eV) [15] and higher than that of Li$_3$N (0.25 eV) [16].
3.2. Sensing characteristics

The sensor is composed of the following electrochemical cell:

\[
\text{Au, } \text{Li}_{0.36}\text{WO}_3|\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}|\text{Li}_2\text{CO}_3, \text{Au, } \text{CO}_2, \text{O}_2
\]

where, I and II show the interfaces between two component materials contacted to one another. The following reactions 4 (interface I) and 5 (interface II) could be used to describe the measured EMF of the sensors.

\[
\frac{2}{3}\text{Li}_{0.36}\text{WO}_3 \leftrightarrow \frac{2}{3}\text{Li}_{0.36-\delta}\text{WO}_3 + 2\text{Li}^+ + 2e^-
\]

\[
2\text{Li}^+ + 2e^- + \text{CO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Li}_2\text{CO}_3
\]

From a microscopic point of view, the sensing reaction processes start at the triple-phase boundary (TPB). The process of O2 and CO2 incorporation has the gas phase into the solid electrolyte is schematically represented in Fig. 5. The process of O2 and CO2 incorporation could be explained by the following proposed steps:

- O2 and CO2 diffusion in the gas phase, and oxygen dissociative adsorption at the surface of Au and at the uncovered surface area of the electrolyte (lithium ion conductor).
- Diffusion of adsorbed oxygen along the surface of Au to the TPB.
- Transfer of electrons to form O\text{ad}^- and O^2- along the diffusion path of the Au surface.
- Diffusion of lithium ions in the electrolyte and electrons in Au to the triple-phase boundary, within the contact zone to react with O^2- and CO2 to form Li2CO3.

During sensing CO2 gas, lithium ions partially released from Li0.36WO3 and transferred through the solid state electrolyte Li6BaLa2Ta2O12. Meanwhile, CO2 molecules easily diffused into the porous auxiliary layer of the sensor, leading to quick adsorption and desorption of CO2 on the reactive sites (TPB) and then to equilibrium with lithium ions and O2 into Li2CO3. The overall cell reaction can be given by Eq. (6).

\[
\frac{2}{3}\text{Li}_{0.36}\text{WO}_3 + \text{CO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{Li}_2\text{CO}_3 + \frac{2}{3}\text{Li}_{0.36-\delta}\text{WO}_3
\]

3.3. CO2 sensing properties

The EMF measurements were performed at 450 and 500 °C by changing the CO2 concentration from 0.01% to 10%. The results are shown in Figs. 6 and 7. The sensor showed a reproducible response with response time (defined as time taken to reach 90%
of the stable signal) of less than 1 min, as shown in Figs. 6 and 7. The faster response time is could be due to the ionic fast kinetics of electrode reactions at the area of the triple-phase boundary (TPB). The sensitivities of the linear fit were 73 mV/decade (calculated sensitivity is 72 mV/decade) and 75 mV/decade (calculated sensitivity is 76 mV/decade) at 450 and 500 °C, respectively. Fig. 8 shows the dependence of EMF as a function of log of CO2 concentration (logpCO2) at 450 and 500 °C. The sensitivities of cells agree within the experimental error with the calculated ones from Nernst’s equation for a two-electron process. The sensitivity to CO2 translated to the nominal number of electrons involved in the cell reaction, provides a value 1.96 at 450 °C and 2.02 at 500 °C (Fig. 8). It is obvious that the slope became larger with the increase of the working temperature, due to the improvement of the ionic kinetics at the effective area of the triple-phase boundary (TPB). This also indirectly indicates that the rate of the electrochemical reaction has been improved in the effective area of the TPB, although the reference electrode is same. The EMF is a linear function of logCO2 partial pressure over the investigated temperature range of 300–500 °C (Fig. 9). And the nearly no deviation from the theoretical slope indicates that there is no electronic conduction is present in the Li6BaLa2Ta2O12 electrolyte during the EMF measurement [17].

It should be mentioned that two main factors play the key roles in determining the rates of the electrochemical reaction of this device [18]: (i) high electrochemical catalytic activity of the sensing electrodes to CO2 and (ii) microstructure of the TPB. In order to testify it, during operating the cell at elevated temperatures, impedance spectroscopy was applied. Fig. 10 shows the complex impedance plots at 450 and 500 °C. The total conductivities were found to be 6.5 × 10^{-4} S cm^{-1} at 450 °C and 8 × 10^{-4} S cm^{-1} at 500 °C. The capacitances as evaluated from the complex impedance plots were 29 nF and 27 nF at 450 °C and 500 °C, respectively. AC impedance as a function of time is shown in Fig. 11. The corresponding interfacial capacitances as evaluated from the complex impedance plots was found to be 21 nF at day 3 and 9.4 nF at day 19. During aging, the total conductivities increased with aging time, suggesting that the contact between the sensing electrode and electrolyte was improved considerably. A similar phenomenon was also reported by Song et al. [19]. This better contact between electrode and electrolyte results is enhanced interfacial adherence, and hence, improved charge transfer kinetics. The sensing electrode reaction (Eq. (5)) requires the reaction of lithium ions from the electrolyte, electrons from the electronic lead, CO2 from the gas phase and O2 from a dissociated oxygen molecule in the gas phase, in a single reaction step. At lower temperatures this reaction may not be kinetically favorable and intermediate products
with less negative Gibbs energies of formation may be formed. This may cause the sluggish response, especially at lower temperatures, where the formation of Li₂CO₃ is impeded by slow electrode kinetics. The discrepancy of 1.5 mV/decade at 300–400 °C may be due to this reason. The sensitivity to CO₂ increased gradually with temperature also suggesting that the in situ formation of Li₂CO₃ is kinetically favorable only at high temperature whereas at intermediate or low temperatures the intermediate compound lithium oxide is formed at the measuring side. These results suggest that the microstructure of an auxiliary layer for solid-electrolyte gas sensors is highly effective for improving the gas sensor properties.

Fig. 12 demonstrates the high stability of the response of the cell to 1% CO₂ in dry synthetic air over elapsed periods of time. During the aging time, EMF of the sensor always keeps on ~237 mV. The long-term stability test of several cells showed, after aging of the sensors, further shift of the absolute value of the open circuit voltage between 2 mV and 8 mV per month. This behavior is well known for this kind of sensor which relies on in situ reaction in the electrode and assumed due to loss of Li₂CO₃ at the TPB [20].

4. Conclusions

The performance of a novel CO₂ sensor based on the garnet-like Li₆BaLa₂Ta₂O₁₂ solid electrolyte and Li₁₀.36WO₃ reference electrode operating at 300–500 °C was investigated. The sensor showed a long-term stable performance and the signa was found to be reproducible. The sensor showed high sensitivity (73 mV/decade) for CO₂, fast response and recovery time, and acceptable long-term stability. With the realization of miniature structure and lower heating temperature, the power consumption was effectively decreased in comparison with the traditional tube-type sensors. AC impedance analyses suggest that the microstructure an auxiliary layer for solid-electrolyte gas sensors is highly effective for improving the gas sensor properties.

Acknowledgments

The financial support of Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (2010-149) and Natural Scientific Research Innovation Foundation in Harbin Institute of Technology (HIT.NSRIF.2011099) is gratefully acknowledged.
conducting lithium ion conducting \( \text{Li}_x\text{BaLa}_2\text{Ta}_2\text{O}_{12} \) solid electrolyte, Solid State Ionics 23 (1987) 107–112.


V. Thangadurai, H. Raack, W. Weppner, Novel fast lithium ion conduction in garnet-type \( \text{Li}_x\text{BaLa}_2\text{Ta}_2\text{O}_{12} \) (M = Nb, Ta), Journal of the American Ceramic Society 86 (3) (2003) 437–440.

V. Thangadurai, W. Weppner, \( \text{Li}_x\text{Al}_{1-x}\text{Nb}_2\text{O}_{12} \) (A = Ca, Sr, Ba): a new class of fast lithium ion conductors with garnet-like structure, Journal of the American Ceramic Society 82 (2002) 411–418.

V. Thangadurai, W. Weppner, Effect of sintering on the ionic conductivity of garnet-related structure \( \text{Li}_x\text{La}_2\text{Nb}_2\text{O}_{12} \), and I- and K-doped \( \text{Li}_x\text{La}_2\text{Nb}_2\text{O}_{12} \), Journal of Solid State Chemistry 179 (2006) 974–984.

V. Thangadurai, W. Weppner, \( \text{Li}_x\text{Al}_{1-x}\text{Ta}_2\text{O}_{12} \) (A = Sr, Ba): novel garnet-like oxides for fast lithium ion conduction, Advanced Functional Materials 15 (1) (2005) 107–112.

V. Thangadurai, W. Weppner, Investigations on electrical conductivity and chemical compatibility between fast lithium ion conducting garnet-like \( \text{Li}_x\text{BaLa}_2\text{Ta}_2\text{O}_{12} \) and lithium battery cathodes, Journal of Power Sources 142 (2005) 339–344.


R. Murugan, V. Thangadurai, W. Weppner, Effect of lithium ion on the lithium ion conductivity of the garnet-like structure \( \text{Li}_{0.5+x}\text{BaLa}_2\text{Ta}_2\text{O}_{12.5+x} \) for \( x = 0–2 \), Applied Physics A 91 (2008) 615–620.


Biographies

Dr. Yongming Zhu received the M.Sc. degree in material engineering from Department of Engineering at Kiel University, Germany, in 2003. He received his Ph.D. degree in the group of solid state ionics and sensors at Kiel University, Germany, with Prof. Werner Weppner, in 2007. Now he is an associate professor at Harbin Institute of Technology (Weihai). His current research is solid electrolyte gas sensor.

Dr. Venkataraman Thangadurai is an associate professor of chemistry at the University of Calgary in Canada. He has received his Ph.D. from the Indian Institute of Science (IISc.), Bangalore, India, in early 1999. His doctoral degree thesis was supervised by professors J. Gopalakrihanan and A.K. Shukla. He did his postdoctoral research at the University of Kiel, Germany, with Prof. W. Weppner. He has received his habilitation degree from the University of Kiel in 2004. He has published over 80 papers in refereed journals on solid state materials, 2 book chapters, and 2 patent applications. He is a member of Editorial Board of the International Journal of Ionics, active member of the Electrochemical Society, and a member of International Society of Electrochemistry.

Dr. Werner Weppner holds since 1993 the Chair for Sensors and Solid State Ionics at the Faculty of Engineering of Christian Albrechts University, Kiel, Germany. He has been earlier at the Max-Planck-Institute for Solid State Research, Stuttgart and a Research Professor at Stanford University, CA, USA, in the Department of Materials Science and Engineering. Prof. Weppner holds a diploma in physics from Mainz University and a Ph.D. in chemistry from Dortmund University, both Germany. His research interests are focused on ion transport in solids and include both fundamental understanding and practical application aspects.