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LISICON GLASS-CERAMICS MEDIATED CATALYSIS OF OXYGEN REDUCTION (POSTPRINT)

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14. ABSTRACT The role of lithium aluminum germanium phosphate (LAGP) glass-ceramic (a lisicon structure) on catalysis of the oxygen reduction reaction (ORR) is investigated by conducting thermo gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) and cyclic voltammetry (CV) measurements. The analysis of the CV data reveals that the LAGP glass-ceramic possesses some inherent catalytic activity toward reduction of oxygen. However, the data also suggest an irreversible nature of the reaction. The TGA and BET data complement the CV results. The Lisicon family of materials appears to be an attractive catalyst for ORR.					
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Lisicon Glass-Ceramics Mediated Catalysis of Oxygen Reduction

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The role of lithium aluminum germanium phosphate (LAGP) glass-ceramic (a lisicon structure) on catalysis of the oxygen reduction reaction (ORR) is investigated by conducting thermo gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) and cyclic voltammetry (CV) measurements. The analysis of the CV data reveals that the LAGP glass-ceramic possesses some inherent catalytic activity toward reduction of oxygen. However, the data also suggest an irreversible nature of the reaction. The TGA and BET data complement the CV results. The Lisicon family of materials appears to be an attractive catalyst for ORR.

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The Lisicon (lithium super ionic conductor) glass-ceramics is a polycrystalline analogue of Nasicon (sodium super ionic conductor) structure. The general class of Nasicon structures consists of two polyhedral, PO_4 and MO_6 ($M = \text{Ti, Ge, Si, etc.}$) linked by their corners to form a rigid $[\text{M}_2(\text{PO}_4)_3]^-$ skeleton. Three dimensional skeletons provide a channel through which Li^+ or Na^+ can migrate. In the Lisicon structure, there are two different sites— A_1 and A_2 which can be occupied by Li^+ . In $\text{LiM}_2(\text{PO}_4)_3$, the A_1 site is fully occupied, whereas the A_2 site is completely vacant. When the tetravalent site M (Ge, Si, Ti, etc.) is substituted for by trivalent (Al^{3+}) ions, charge compensation is required. The requirement is met by an incorporation of additional lithium ions. The additional lithium ions occupy the A_2 sites which are critical for enhancing conductivity of the Lisicon materials.

A typical Lisicon structure of $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)$, Figure 1 shows existence of cavities and tunnels. The structure facilitates transport of Li^+ and can also accommodate a gaseous phase such as molecular oxygen. In this context, the Lisicon structure resembles the structure of well-known zeolites. It is conceivable that in addition to an ability to transport Li^+ , the Lisicon structure can also facilitate catalysis of molecular species; for example reduction of oxygen. In fact, such an attribute of the Lisicon structure was successfully used in the fabrication of Li-O_2 cell.¹ Subsequently, the role of the Lisicon structures, $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)$ was delineated in the cathodes of the Li-O_2 cell.² It was suggested that the structure possesses an inherent tendency to absorb oxygen molecules. The absorption was followed by reduction of oxygen.

Glass-ceramics (GC) are a polycrystalline material generally formed by the conventional glass making process followed by a nucleation and crystallization thermal treatments. Fu (Refs. 3 and 4) reported processing and characterization of lithium ion conducting glass-ceramics in the $2[\text{Li}_{1-x}\text{Ti}_2\text{Si}_2\text{P}_{3-x}\text{O}_{12}]\text{-AlPO}_4$ system. Lithium aluminum germanium phosphate, $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}\text{PO}_4$ also abbreviated as LAGP has received considerable attention during the last decade as an electrolyte for lithium batteries.⁵

This paper presents and discusses oxygen reduction reaction (ORR) by the LAGP glass-ceramic in an alkaline, 0.1 M KOH medium around the ambient temperature. The paper reports data on thermo gravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface area, and cyclic voltammetry (CV) measurements which lead to a conclusive evidence of catalysis.

chemicals such as Li_2CO_3 (Alfa Aesar), Al_2O_3 (Aldrich, particle size <10 nm), GeO_2 (Alfa Aesar), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Acros Organics). The chemicals were weighed, mixed, and ground for 10 min with an agate mortar and pestle. For further homogenization, the batch was milled in a glass jar for 1 h using a roller mill. The milled batch was contained in a platinum crucible and transferred to an electric furnace. Initially, the furnace was heated to 350°C at the rate of $1^\circ\text{C}/\text{min}$ and held at that temperature for 1 h to release the volatile components of the batch before raising the furnace temperature to 1350°C at the rate of $1^\circ\text{C}/\text{min}$ after which the glass was melted for 2 h. A clear, homogeneous, viscous melt was poured onto a stainless steel (SS) plate at room temperature and pressed by another SS plate to yield <1 mm thick transparent glass sheets. The glass specimens were crystallized in the $750\text{--}850^\circ\text{C}$ temperature range for selected times. The plates of GC were crushed and ground to powder with particle size $<50\text{ }\mu\text{m}$. The powder was used for TGA, BET, and CV measurements.

Thermal characterization was conducted on approximately 10 mg of LAGP specimen using TGA (TA Instruments, model 2050). The specimens were placed on the holder and contained in the chamber maintained with the normal atmosphere. The sample was heated from room temperature to 1000°C with a heating rate of $5^\circ\text{C}/\text{min}$.

In the BET technique a dry specimen was evacuated of all gases and cooled down to 77 K, liquid nitrogen temperature using a nitrogen sorption instrument (Micromeritics ASAP 2020). Nitrogen gas was then introduced in the specimen chamber. A layer of the gas physically adhered to the specimen surfaces resulting in the lowering of the chamber pressure. This allowed measurement of adsorption isotherms and computation of specimen pore size and surface area.

CV measurements were conducted using three-electrode cell. The pyrolytic graphite electrode was coated with a mixture of LAGP (1 mg) and 5% Nafion (1 ml) to serve as a working electrode. A Pt wire and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The electrolyte, 0.1 M KOH was bubbled with oxygen or nitrogen during the measurement. The electrochemical measurements were performed with a Solartron Instrument (Model 1287 with electrochemical interface) controlled by a computer. All potentials were measured with respect to SCE. The scan rate during measurement was $5\text{ mV}/\text{s}$.

Experimental

A 40 g batch of 19.75 Li_2O , 0.617 Al_2O_3 , 37.04 GeO_2 , 37.04 P_2O_5 (mol %) composition was prepared by using reagent-grade

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Results and Discussion

Figure 2 shows TGA data of two LAGP specimens—as received and heat treated in a vacuum oven at 100°C . The LAGP powder used as specimen was prepared in the normal atmosphere and therefore some interaction with/or adsorption of atmospheric gases was expected. However, it is noted from the TGA profile of the as-

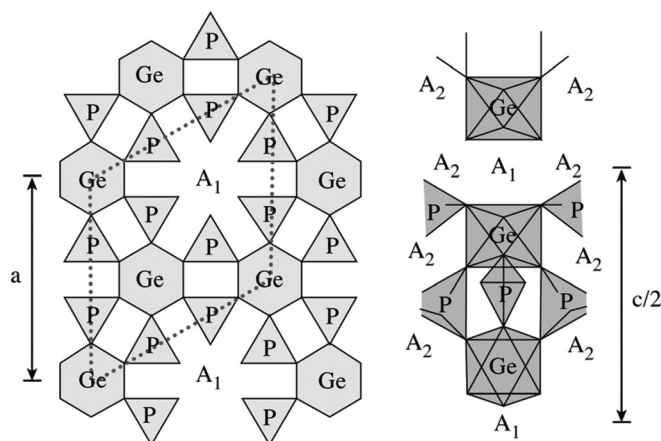


Figure 1. Lisicon structure (not drawn to scale). (a) planar view showing only A₁ sites and, (b) three-dimensional view showing both A₁ and A₂ sites.

received specimen that the weight loss is approximately 2.4% when heated up to about 500°C. After the specimen was heat treated at 100°C in a vacuum oven the weight loss was reduced to 1.00%. It is apparent that the specimen lost 1.4 wt % by a simple heat treatment in a vacuum oven. The observation points out existence of mesoporous structure of LAGP and its inherent ability to adsorb gases. If it is assumed that the weight loss arises from the adsorbed air (N₂, O₂, H₂O, CO₂) then the volume of air is approximately 21 cc (0.024/0.001161)^d per gram of the LAGP. This large retention volume within the LAGP glass-ceramic can be used to contain and catalyze certain gases, for example oxygen in the mesoporous structure.

Mass spectroscopy of the gases evolved from the LAGP specimen was conducted. The data revealed presence of all the constituents of air (N₂, O₂, H₂O, CO₂). However, quantitative analysis for their relative proportion could not be obtained because of small specimen size.

Several BET measurements on the specimen revealed a pore size distribution from 0.90 to 2.80 nm and surface area of about 0.40 m²/g. It should be noted that even the lower end of the pore size distribution is capable of accommodating gaseous molecules of the ambient atmosphere. In Fig. 2, the TGA analysis clearly shows that the gases are released when heated to higher temperatures. The surface area of the specimen, 0.40 m²/g is small compared to other catalytic materials such as activated carbon. However, it should be appreciated that the present LAGP specimen was not synthesized to optimize the surface area. In fact, the processing parameters of the LAGP were designed such that the material provided the highest density (lowest porosity and surface area).

Shown in Fig. 3 are CVs of the LAGP and Ketjen black (KB) specimens with reference to the SCE electrode (0.242 V). In the case of LAGP the electrolyte, 0.1 KOH was bubbled with N₂ and O₂. As expected, no electrochemical activity is noted when electrolyte was bubbled with nitrogen. Well defined cathodic and anodic peaks located at -0.6 and 0.5 V respectively are evident when the electrolyte was bubbled with oxygen. It is noted that the KB curve exhibits a peak at -0.27 V. The LAGP peaks are distinctly different (inset, Fig. 3) in terms of their locations and significantly stronger in their intensities. These are major electrochemical activity. The cathodic and anodic peak intensities are 1.4 and 0.9 mA/cm², respectively. An asymmetry in the peak locations and intensities points out a possibility of irreversibility of the reactions. The criteria for reversibility of a reaction from the CV data are often expressed in terms of equal cathodic (*i*_{pc}) and anodic (*i*_{pa}) peak current densities and the difference in corresponding potentials, Δ(*E*_{pa} - *E*_{pc}) = (59/*n*) mV; where

^dDensity of air at 300 K, Hand book of Physics and Chemistry, 73rd Edition.

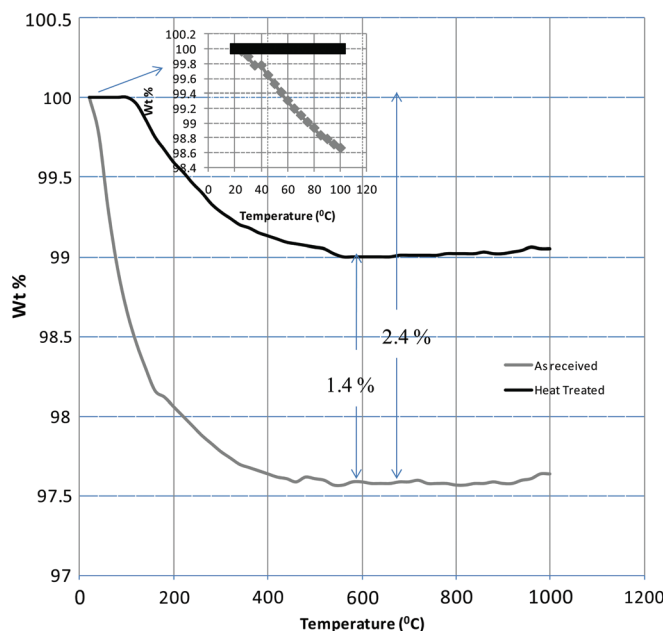


Figure 2. (Color online) Thermogravimetric analysis of LAGP powder with inset being an expanded view of TGA analysis up to 100°C.

*E*_{pc}, *E*_{pa}, and *n* are cathodic potential, anodic potential and number of electrons participating in the reaction. The *i*_{pa}/*i*_{pc} ratio and Δ(*E*_{pa} - *E*_{pc}) are 1.6 and 1.1 V. For the reversible reaction the *i*_{pa}/*i*_{pc} ratio and Δ(*E*_{pa} - *E*_{pc}) should be 1 and 0.015 V, respectively. The irreversibility of the reaction may stem from kinetic hindrance to the transport of O₂ and Li⁺ and asymmetric activation energy for the involved reactions. In spite of the irreversible nature of the reaction, data of Fig. 3 clearly demonstrate LAGP mediated ORR.

Conclusion

A Lisicon GC of a 19.75 Li₂O, 0.617 Al₂O₃, 37.04 GeO₂, 37.04 P₂O₅ stoichiometry was formulated, synthesized, and characterized by TGA, BET, and CV. TGA data revealed desorption of about 2.4 wt % of gaseous species from the material when heated up to

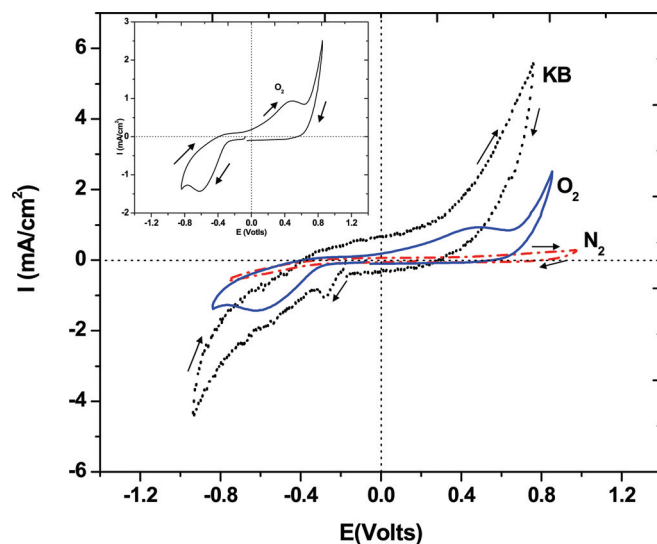


Figure 3. (Color online) Cyclic voltammogram from the LAGP (O₂ and N₂) and KB (O₂) specimens in 0.1 M KOH; sweep rate = 5 mV/s, T = 25°C. Inset shows the CV of LAGP (O₂).

500°C. The pore size in the GC varied from 0.90 to 2.80 nm and surface area of the specimen was 0.40 m²/g. The mesoporous structure allowed adsorption of atmospheric gases during processing of the specimen. The amount of adsorbed gases is significant, approximately 21 cc per gram of LAGP powder. This attribute of the material makes it suitable for catalysis. In view of the attribute, the GC specimen was characterized by CV. The CV data clearly demonstrated existence of cathodic and anodic peaks located at -0.6 and 0.45 V vs SCE as catalyzed by the Lisicon GC. The evidence of ORR by the LAGP material is clear; however, the nature of reduction appears to be irreversible.

Oxygen reduction is a fundamental electrochemical reaction. It is the reaction around which several industrial products and processes (fuel cell, batteries, oxygen separation membranes, sensors) are designed. It is also known that the ORR is sluggish often requiring use of expensive (precious metals) catalysts and high temperature. The discovery of catalytic property of Lisicon structures presents an opportu-

nity to assess its usefulness in the industrial products to improve upon their performance.

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