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In celebration of the 60th birthday of Dr. Andrew K. Galwey

THE DOPING EFFECT OF ALTERVALENT CATIONS ON THE THERMAL DECOMPOSITION AND ELECTRICAL CONDUCTION PROPERTIES OF MANGANESE(II) CARBONATE

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Abstract

The electrical conductivities of pure and doped manganese(II) carbonate with 10 mol% Li^+ or Al^{3+} ions were measured. The effect of doping on the observed kinetic parameters of decomposition were measured. Doping with Li^+ or Al^{3+} ions enhances the decomposition. The enhanced promotion effect is ascribed to the generation of hole defects which are concentrated at the reaction interface.

Keywords: doping effect, electrical conductivity, manganese(II) carbonate, TD-DTA, X-ray

Introduction

Considerable importance has been focused on the thermal analysis of solid carbonates [1] which yield pure or mixed oxides used as active catalysts. Data obtained made it possible to propose a diffusion-kinetic model of moving fronts, based on the positive feedback that arises during the course of reaction as the stresses occurring in the vacancy structure relax and porous reaction products form [2].

Manganese(II) carbonate, as a parent material [3] for manganese oxides, has received few studies of the effect of additives on the kinetics and mechanism of decomposition. It is known that doping with altervalent metal oxides change surface [4], electrical [5] and catalytic properties [6] quite significantly. Hence, our present work is concerned with measurements of the electrical conductivity of pure and doped manganese carbonate with relation to the solid state decom-

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position process. These measurements were supplemented with data obtained by TG, DTA, X-ray diffraction and IR spectra analysis.

Experimental

Analar manganese(II) carbonate was used as a parent material for thermal decomposition experiments and for preparing the doped salts. Li^+ and Al^{3+} nitrates were used as dopant ions in concentration of 10 mol%, using the impregnation method. The impregnated specimens were calcined in air at different temperatures up to 1000°C for measurements of non-stoichiometry.

TG and DTA were conducted using a Rigaku microbalance model 220219 with a heating rate of 10 $deg \cdot min^{-1}$, in air atmosphere, and 20 mg sample mass, up to 800°C. X-ray diffraction patterns for the product oxides were obtained with a Philips unit type 1010 using CuK_α radiation of wave length 1.5428Å. IR spectra were obtained using a Perkin Elmer spectrophotometer, model 20, in the range 1800–400 cm^{-1} using the KBr disc technique. Non-stoichiometry of the product oxides was determined by the hydrazine method by adopting the method of Uchijima *et al.* [7]. Conductance measurements were carried out, using a cell described by Chapman *el al.* [8], in the temperature range 25–250°C as previously described [9].

Table 1 Thermal decomposition data for pure manganese(II) carbonate and samples doped with Li^+ or Al^{3+} ions, in air atmosphere

Compound	Peak temperature from DTA				Mass loss / %
	I	II	III	IV	from TG
Manganese(II) carbonate	–	241	415	641	38
doped with					
10 mol% Li	–	231	405	615	51.4
10 mol% Al	130	235	418	630	47.3

Results and discussion

Figures 1–3, show the TG and DTA curves of pure and doped manganese(II) carbonate with 10 mol% Li^+ and Al^{3+} ions. Three endothermic peaks were recorded in the range 200–800°C. Addition of Li^+ and Al^{3+} ions increases the percentage decomposition and lowers the peak temperatures of the endotherms. The doping effect of Li^+ ions is more pronounced than Al^{3+} ions, as cited in Table 1.

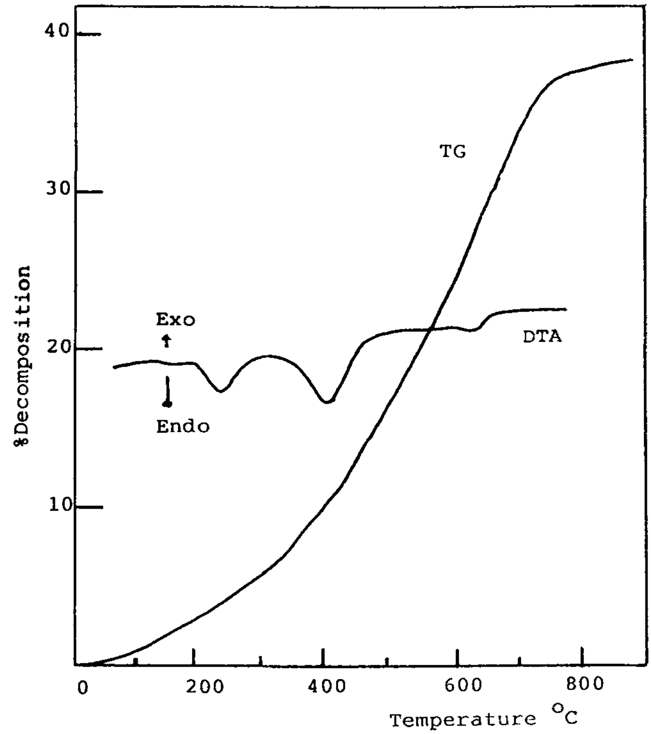

Fig. 1 TG and DTA curves for manganese(II) carbonate in air

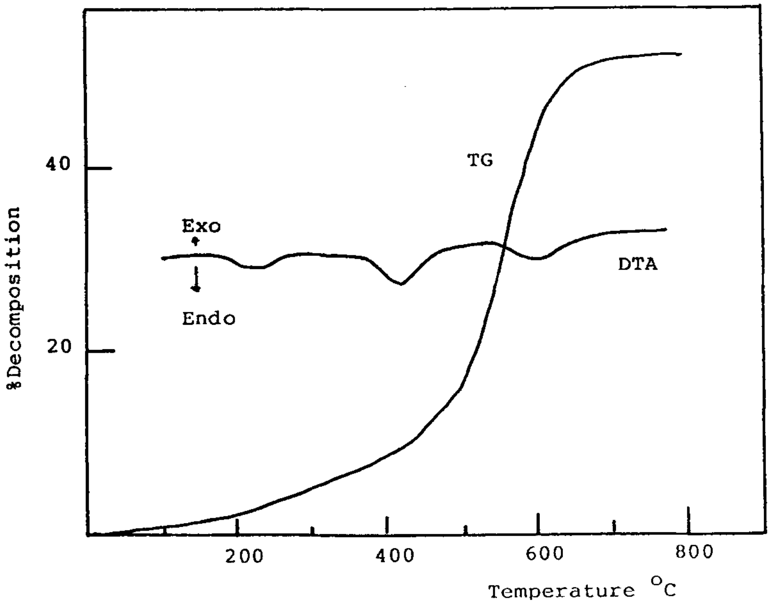

Fig. 2 TG and DTA curves for manganese(II) carbonate doped with 10 mol% Li^+ ions

Table 1, shows a higher percentage mass loss when manganese(II) carbonate is doped with Li^+ than with Al^{3+} ions, due to the creation of solids defective in oxygen content [9]. Their non-stiochiometry was determined as shown in Fig. 4. Curve (a) shows continuous variation of the excess surface oxygen con-

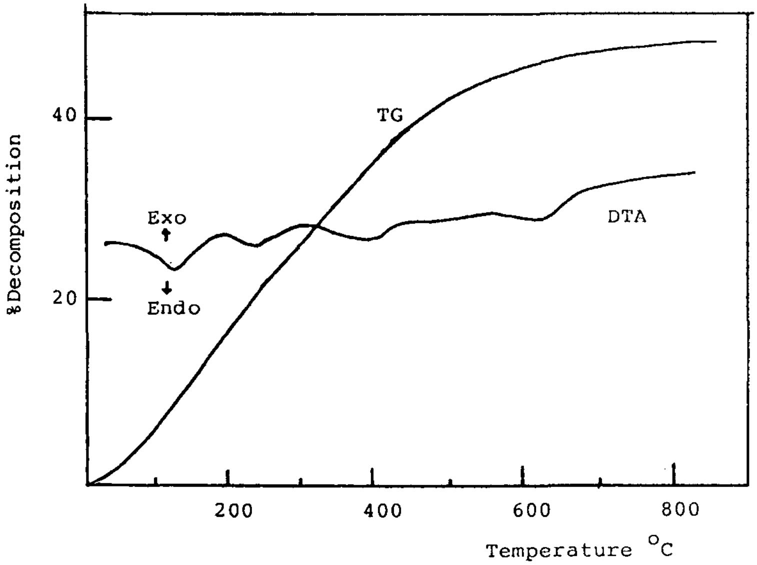

Fig. 3 TG and DTA curves for manganese(II) carbonate doped with 10 mol% Al^{3+} ions

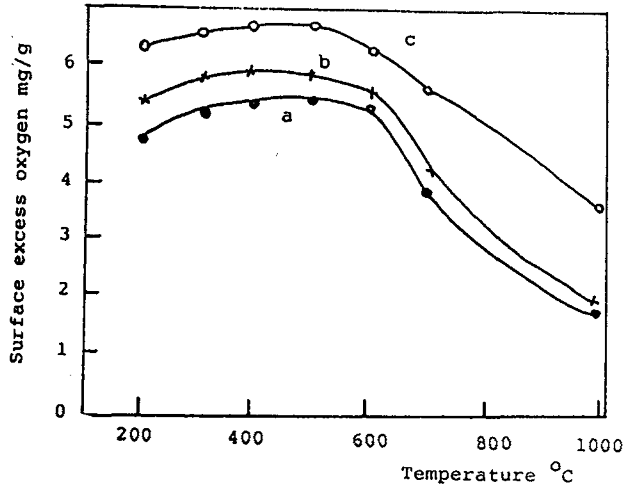

Fig. 4 The amount of surface excess oxygen obtained by the hydrazine method against calcination temperature for pure manganese(II) carbonate (a) and that doped with Li^+ (c) and Al^{3+} (b) ions

tent, followed by an abrupt decrease after 500°C. Doping with Li^+ ions, curve (b) reveals a higher deviation from stoichiometry than when doping with Al^{3+} ions curve (c). This behaviour shows the increased defective lattice structure on doping.

The non-isothermal TG curves for pure and doped manganese(II) carbonate were used to elucidate the decomposition mechanism, adopting the process discussed by Sestak and Berggren [10] and Satava [11]. The procedure is based on the assumption that non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation:

$$\frac{\partial\alpha}{\partial t}=Ae^{-E/RT}f(\alpha) \tag{1}$$

where A is the pre-exponential factor, t is the time and $f(\alpha)$ depends on the mechanism of the process. For a linear heating rate ($Q = dT/dt$) and substitution into Eq. (1), gives

$$\frac{\partial\alpha}{f(\alpha)}=\int_0^T\frac{A}{Q}e^{-E/RT}\partial T \tag{2}$$

Integration of the left-hand side of Eq. (2) gives

$$\int_0^\alpha\frac{\partial\alpha}{f(\alpha)}=g(\alpha)=\int_0^T\frac{A}{Q}e^{-E/RT}\partial T \tag{3}$$

where $g(\alpha)$ is the integrated form of $f(\alpha)$. A series of $f(\alpha)$ forms is proposed by Satava [11] and the mechanism is obtained from that plot which gives the best representation of the experimental data. For evaluating the kinetic parameters from the mechanism equation, the right-hand side of Eq. (3) was used in the Coats-Redfern [12] equation which is recommended in several reports [13, 14]. The general form of the equation used is

$$\ln g(\alpha)/T^2=\ln\frac{AR}{QE}-\frac{E}{RT} \tag{4}$$

Table 2 Kinetic parameters for the decomposition of pure manganese(II) carbonate and that doped with lithium or aluminium ions using the mechanistic equations together with the Coats-Redfern method

Compound	Correlation coefficient	E / kJ·mol^{-1}	ΔS / J·mol^{-1}·K^{-1}	Kinetic model
Manganese(II) carbonate	0.9848	45.34	−113.3	F_n=2
doped with				
10 mol% Li$^+$	0.9793	33.98	−121.5	F_n=2
10 mol% Al^{+++}	0.9922	19.93	−123.3	F_n=2

Values of E obtained from the mechanistic equations along with the correlation co-efficient for the kinetic plots for the TG curves have been evaluated. The entropy change ΔS was calculated using the equation

$$\Delta S = R\ln(Ah/kT) \qquad (5)$$

where k is the Boltzmann constant and h is the Planck constant. The values of the kinetic parameters corresponding to the highest correlation coefficient values were selected and cited in Table 2. The negative ΔS values indicate a more ordered intermediate active state [15].

The data presented in Table 2 show that the thermal decomposition of pure manganese(II) carbonate in air follows the F_n = 2 mechanism and does not change on doping. The low E value obtained for Al doped specimen is attributed to the presence of water which appeared to be removed at 130°C (Fig. 4), thus facilitating the ion mobility for decomposition.

The X-ray diffraction patterns for the decomposition products formed at various temperatures in air are shown in Fig. 5. Up to 400°C β–MnO_2 was formed. Between 500° and 700°C transformation of the β–MnO_2 to Mn_2O_3 ox-

Table 3 IR absorption bands for the calcined products of manganese(II) carbonate

Specimen calcination T / °C	1	2	3	4	5	6
200	1600–1330	850	710	–	–	–
300	1550–1350	855	715	580	–	–
400	1520–1300	860	720	590	–	–
500	–	–	680	620	580	500
700	–	–	670	610	580	530
1000	–	–	–	600	540	480

ide occurred. On further heating, only diffraction lines characteristic of Mn_3O_4 oxide were detected. These results were confirmed through IR spectra as shown in Table 3.

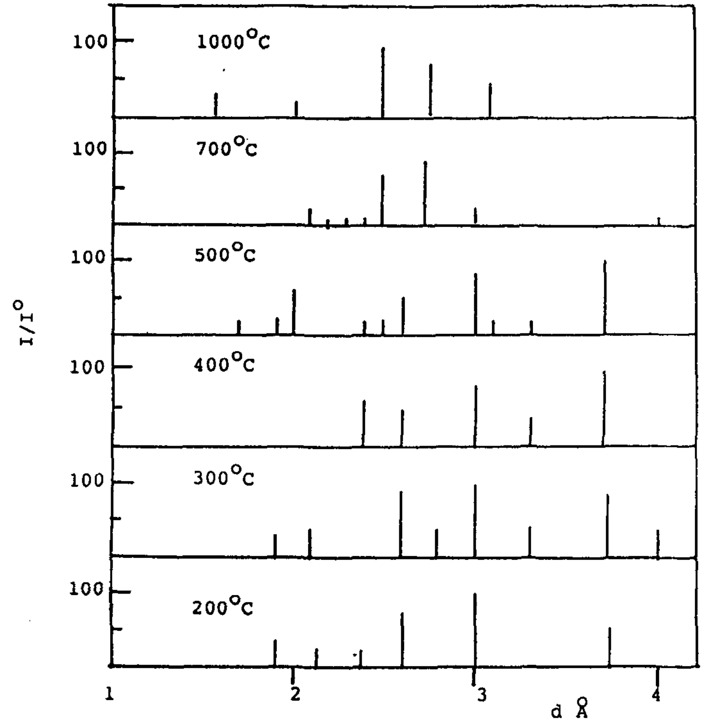

Fig. 5 X-ray diffraction patterns of the calcination products of manganese(II) carbonate in air at different temperatures

It is to be noted that samples calcined up to 400°C have a broad band located in the region of 1600–1300 cm^{-1} followed by two sharp bands at 860 cm^{-1}. The broad band which appeared at 580 cm^{-1} for a specimen calcined at 300°C is attributed to formation of γ-MnO_2. The broad band in the region of 590 cm^{-1}, observed for the sample calcined at 400°C is assigned to a phase transition to β-MnO_2 [15]. For samples calcined at 500°–700°C, new bands were developed at 680–500 cm^{-1} whose intensities increased with calcination temperature. These changes reveal phase transitions of β-MnO_2 to Mn_2O_3 [16, 17]. At 1000°C the absorption band at 600 cm^{-1} was more intense than the peak at 480 cm^{-1} corresponding to development of the Mn_3O_4 lattice [18]. The doping effect on the host lattice, using 10 mol% Li^+ and Al^{3+} ions, did not change the assignment of the vibrational bands of the thermal decomposition products. Such results agree with the transformation temperatures deduced previously by Honda and Stone [19] and with those recorded recently [20].

$$\gamma\text{-}MnO_2 \xrightarrow{400^\circ C} \beta\text{-}MnO_2 \xrightarrow{650^\circ C} Mn_2O_3 \xrightarrow{900^\circ C} Mn_3O_4 \qquad (6)$$

The dc electrical conductivities, on heating the parent materials up to 250°C and cooling, were recorded as log σ, where σ is the specific conductance, as a function of the absolute temperature as shown in Fig. 6. The cooling curves are characterized by a discontiniuity which occurs at different temperatures depending on the nature of the doping ion. The reason can be found in the above investigations of IR spectra and DTA curves which predict lattice transformations [21, 22]. The linear dependence of the conductance on temperature would show the validity of the equation $\sigma = \sigma_o \cdot \exp(-\Delta E/2kT)$, where, assuming the band model is applicable, ΔE can be considered as the activation energy for releasing free carriers. The activation energies measured from the cooling curves in the range of temperature 100–250°C are 43.54, 27.86 and 13.93 kJ/·mol^{-1} for

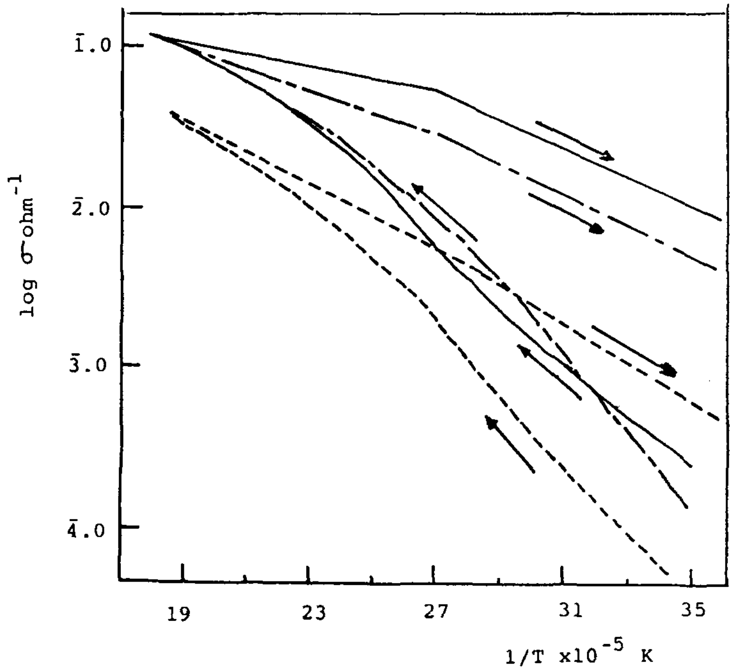

Fig. 6 Variation of the conductance with temperature for manganese(II) carbonate (---) and that doped with 10 mol% Li$^+$(—) and 10 mol% Al^{3+} ions (- — -) on heating (←) and cooling (→)

the decomposition products of pure manganese(II) carbonate and that doped with Al^{3+} and Li^{+} ions, respectively. The low ΔE values on doping are due to the increase of charge carriers. Since manganese oxides are p-type semiconductors [23], a possible explanation for the dependence of the activation energy on the dopant type is given by the following doping mechanisms:
with Li^{+} ion doping

$$3/2\ O_2 + Li_2O = 2Li|Mn|''' + 2MnO_2 + 6[e]^{\cdot} \tag{7}$$

and with Al^{3+} ion doping

$$1/2\ O_2 + Al_2O_3 = 2Al|Mn|' + 2MnO_2 + 2[e]^{\cdot} \tag{8}$$

where $[e]^{\cdot}$ denotes a defect electron and $Li\ |Mn|'''$ and $Al|Mn|'$ are Li and Al ions replacing the manganese ions in lattice positions.

These doping mechanisms indicate that creation [24] of defect electrons within the lattice of the decomposition product will facilitate the electron migration and consequently lead to an enhancing effect on the thermal decomposition process of manganese(II) carbonate.

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Zusammenfassung — Es wurde die elektrische Leitfähigkeit von reinem und versetzten Mangan(II)-karbonat mit 10 mol% Li^+ oder Al^{3+} Ionen untersucht. Dabei wurde der Effekt der Versetzung auf die Zersetzungsparameter der beobachteten Kinetik gemessen. Versetzen mit Li^+ oder Al^{3+} Ionen begünstigt die Zersetzung. Dieser begünstigende Effekt wird der Erzeugung von Lochdefekten zugeschrieben, die an der Reaktionsgrenzfläche gehäuft vorkommen.