

ON THE CATALYTIC PROPERTIES OF MIXED OXIDES FOR THE ELECTROCHEMICAL REDUCTION OF OXYGEN

RAGNAR LARSSON* and LENNART Y. JOHANSSON

Inorganic Chemistry 1, Chemical Center, P.O. Box 124, S-221 00 Lund (Sweden)

(Received June 30, 1989; in revised form March 9, 1990)

Summary

Mixed oxides of the perovskite structure have been synthesized and their efficiency as catalysts for the reduction of oxygen at a carbon electrode in 6 M KOH has been studied. The magnetic susceptibility has been measured for the oxides before use and a formal magnetic moment calculated. No obvious correlation between the measured quantities was found. Possibly some arguments can be given for the existence of a minimum of catalytic effect for magnetic moments of about 1.8 Bohr magnetons. This value is suggested to correspond to the similar quantity of superoxide ion O_2^- , indicating an unfavourable interaction between catalyst and this reaction intermediate having equal number of unpaired electrons.

Introduction

It has been known for many years that mixed oxides of the general type $(A,A')(B,B')O_3$ with a perovskite-related structure have good to fair properties as catalysts for the reaction



Of early investigations on such compounds one can mention those on $LaNiO_3$ [1], $(La_xSr_{1-x})CoO_3$ [2] and $(La_xSr_{1-x})MnO_3$ [3]. Several reviews on the physical properties of perovskite materials are available [4 - 6]. As in most oxides of transition metal atoms with unpaired electrons the magnetic coupling is of great and intriguing importance. The discovery by Hibbert and Tseung [7] that the transition of NiO from the ferromagnetic to the paramagnetic state resulted in a significant increase in the catalytic power of that oxide made the frame of the present work. How important are the magnetic properties for the catalytic activity? Indeed, it has been a

*Author to whom correspondence should be addressed.

matter of some controversy as to whether the catalytic power is caused by 'electronic' or 'magnetic' properties in these systems [5]. This is not a simple question as the magnetic properties so obviously depend on the electronic structure of the system.

In the present investigation we have prepared a series of mixed oxides of perovskite-related structure. We have measured their magnetic susceptibility, specific surface and electrochemical activity. This latter property was taken as the current density at a certain potential of the electrode; a high current density implying a good catalyst, a low one implying a bad catalyst. The reactions were performed using strongly alkaline solutions (6 M KOH).

The origin of catalytic activity is manifold. However, by measuring the magnetic and electrochemical properties of identical preparations of widely varying chemical nature one might trace a functional relationship. (From this approach it is not even too important if the preparations are true perovskites or not.) If such a relationship is found, the magnetic influence is one of the causes of the catalytic effect but not the only one. This cause might act through the interaction between the paramagnetic O_2 molecule (or the O_2^- formed as an intermediate) and the magnetic field originating from the oxide. Such an effect should appear in the preexponential factor of the rate expression as it implies an entropy-related ordering between the reactants. Obviously, the direct contribution to energy terms will be negligible as magnetic forces are much weaker than electrostatic ones.

Experimental

The oxides were prepared following the recommended literature procedure [8, 9], with some slight modifications. The preparations were made by mixing solutions of the metal nitrates in requested proportions, drying and treating the residue at 225 - 300 °C to drive off the nitrogen oxides. Thereafter the oxide materials were calcined at a temperature of 1000 °C for 4 h. The (La,Pb)MnO₃ preparations were made from carbonates of the relevant elements heated at temperatures up to 900 °C for about 10 h.

The magnetic susceptibility was measured on a microcomputer-controlled Cahn RG electrobalance using the Faraday principle. This apparatus has been described in other contexts by Albertsson *et al.* [10]. From this susceptibility a formal magnetic moment was obtained per formula weight. Some substances were collectively magnetic (ferromagnetic, ferrimagnetic or antiferromagnetic) and consequently showed a response on the balance that was dependent on the field used. For these systems we made linear extrapolation to zero magnetic field. Even then the resulting magnetic moments were much higher than one usually encounters for isolated chemical systems. Figure 1 shows an extreme example of such an extrapolation for La_{0.7}Pb_{0.3}MnO₃ and La_{0.8}Pb_{0.2}MnO₃.

The electrochemical measurements were made with a half-cell arrangement described before [11] that allowed the use of very small amounts of

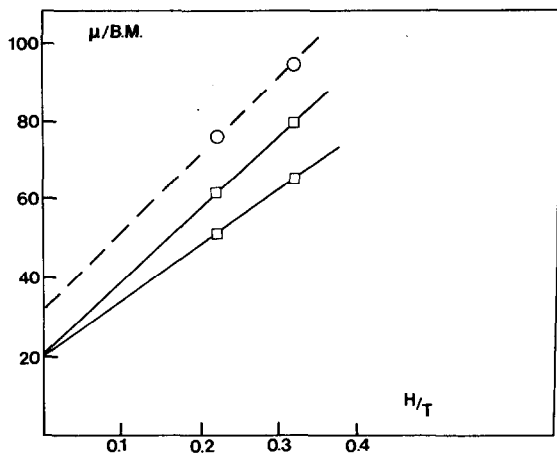


Fig. 1. Example of the procedure for extrapolating the measured magnetic moment to zero field strength of the magnetometer when studying collectively magnetic species: $\text{La}_{0.8}\text{Pb}_{0.2}\text{MnO}_3$, \circ ; $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$, \square . The two lines represent two different preparations at somewhat different temperatures.

material. Therefore the current densities in no way indicate the maximum capability of the catalysts. The cell arrangement is shown in Fig. 2. The electrode was made up in the following way. A mixture of 50% (by weight) of the oxide and 50% of a carbon black (Philblack 1- 1SAF) was ground in a small ball mill for 10 min. Thereafter a few drops of ethanol was added to the mixture and the suspension was applied on a porous PTFE sheet in an even layer. The PTFE sheet was dried at 100°C for 5 min. It was weighed before and after the addition of the catalyst mixture. The catalyst-PTFE

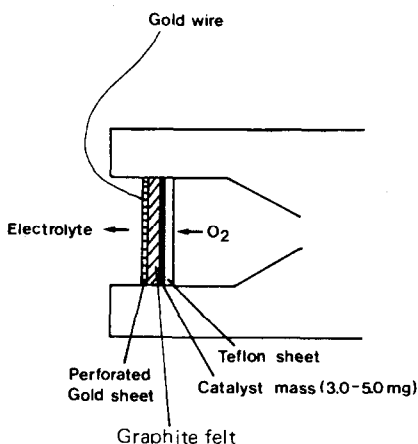


Fig. 2. The electrode arrangement. The depicted unit is dipping into the electrolyte solution, the gold wire is one pole and a platinum wire on the other side of a glass frit is the other. The reference electrode is in close vicinity to the investigated electrode via a Luggin capillary. Pure oxygen is slowly bubbled through the porous electrode out into the electrolyte solution.

sheet was mounted in a holder together with a piece of graphite felt (PE 204 Sigri Elektrographit GmbH) to prevent the catalyst from being dispersed into the electrolyte. A perforated gold plate was used as a current collector. Pure oxygen was passed through the electrode into the electrolyte. It was checked that with this arrangement the current density — expressed as mA/mg catalyst mixture — was independent of the amount of catalyst.

The procedure of measurement was the following. The open cell voltage was measured after the start of the oxygen bubbling, then an initiating (forming) process of the electrode was made so that current was drawn from the system at a potential of -20 mV *versus* Hg/HgO for a period of 30 min. During this time the current was occasionally measured. Following this, the open cell voltage was measured at intervals during a new 30 min period. Thereafter the current was measured at decreasing values of the potential *versus* Hg/HgO with 10 mV intervals, Finally the procedure was reversed, *i.e.*, the current was measured while stepping the potential back to the original value. There was a slight hysteresis for some of the preparations for the curves registered when reversing the sweep as described. The results reported here, however, are the mean values of the readings in the forward and return modes.

Typical polarization curves are represented in Fig. 3. No clear region of Tafel behaviour could be found, indicating the complexity of the reaction.

The specific area of the preparations was determined with an Areameter (Ströhlein & Co) according to the method developed by Haul and Dumbgen [12]. The numbering of the oxides to be used in subsequent figures and the measured specific area are presented in Table 1.

Results

As an indication of the catalytic activity of the oxides we have used the current density measured at the electrode potential -20 mV *versus* the

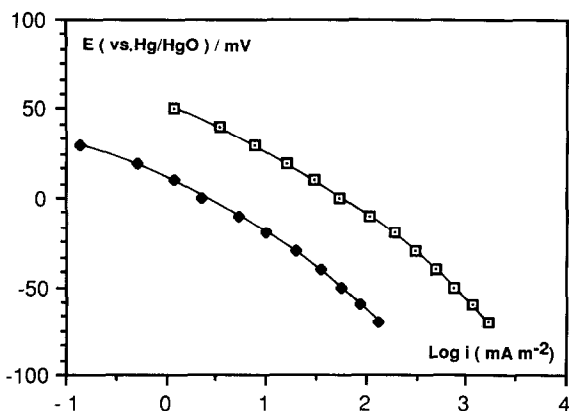


Fig. 3. Two representative examples of the polarization curves. The upper curve represents $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ and the lower one represents $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$. In both cases the points represent the mean value for both directions of sweep.

TABLE 1

Numbering and specific area of the oxide systems used as catalysts in the present investigation

Number	Oxide system	Specific area ($\text{m}^2 \text{g}^{-1}$)	$\log i$ (mA m^{-2})	Magnetic moment (BM)
1	$\text{Ca}_{0.5}\text{Sr}_{0.4}\text{La}_{0.1}\text{MnO}_3$	9.6	1.59	7.7
10	$\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$	1.0	2.26	4.4
11	$\text{La}_{0.1}\text{Sr}_{0.9}\text{CoO}_3$	0.6	2.41	5.5
13	$\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$	1.9	2.13	6.9
14	$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	1.0	2.40	9.6
20	$\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_3$	2.9	1.49	5.8
21	$\text{LaMn}_{0.1}\text{Cu}_{0.9}\text{O}_3$	1.0	0.90	1.8
22	$\text{LaMn}_{0.5}\text{Cu}_{0.5}\text{O}_3$	1.1	1.36	4.3
23	$\text{LaMn}_{0.3}\text{Cu}_{0.7}\text{O}_3$	1.1	1.19	3.1
24	$\text{LaMn}_{0.7}\text{Cu}_{0.3}\text{O}_3$	2.0	1.41	5.0
30	$\text{LaMn}_{0.7}\text{Cr}_{0.3}\text{O}_3$	3.0	1.37	2.5
31	$\text{LaMn}_{0.1}\text{Cr}_{0.9}\text{O}_3$	4.8	1.16	2.8
32	$\text{LaMn}_{0.9}\text{Cr}_{0.1}\text{O}_3$	3.5	1.28	8.1
34	$\text{LaMn}_{0.5}\text{Cr}_{0.5}\text{O}_3$	3.1	1.29	8.3
35	$\text{LaMn}_{0.3}\text{Cr}_{0.7}\text{O}_3$	3.7	1.13	11.3
40	LaNiO_3	2.0	1.56	1.3
50	$\text{LaMn}_{0.3}\text{Ni}_{0.7}\text{O}_3$	2.8	1.77	6.9
51	$\text{LaMn}_{0.5}\text{Ni}_{0.5}\text{O}_3$	2.4	1.00	13
60	SrMnO_3	1.7	1.73	2.9
70	$\text{Eu}_{0.2}\text{Sr}_{0.8}\text{MnO}_3$	3.4	1.63	4.0
71	$\text{Eu}_{0.4}\text{Sr}_{0.6}\text{MnO}_3$	4.3	1.42	4.4
73	$\text{Eu}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$	0.7	2.01	4.9
80	$\text{Eu}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$	3.7	1.89	4.8
81	$\text{Eu}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$	4.6	1.88	5.9
90	$\text{La}_{0.8}\text{Pb}_{0.2}\text{MnO}_3$	3.9	1.60	32
91	$\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$	5.2	1.00	20

Hg/HgO reference electrode. The results are given in Table 1 and also in graphical form in Figs. 4 and 5. Figure 4 represents a series of very similar oxides, viz. $\text{LaMn}_x\text{Cu}_{1-x}\text{O}_3$. Figure 5 gives an overview of all the measured systems.

Discussion

The result given in Fig. 4 can be said to represent the difficulty in separating the magnetic and electronic effects. Within this series of nearly related oxides there is obviously a linear relationship between the properties in question. Probably the magnetic moment is more important in this connection than, say, for example, the UV spectroscopic parameters but they are all interrelated. One can notice from Fig. 5 that the also closely related systems nos. 30, 31, 32, 34, 35 also follow a linear relation but with a negative slope.

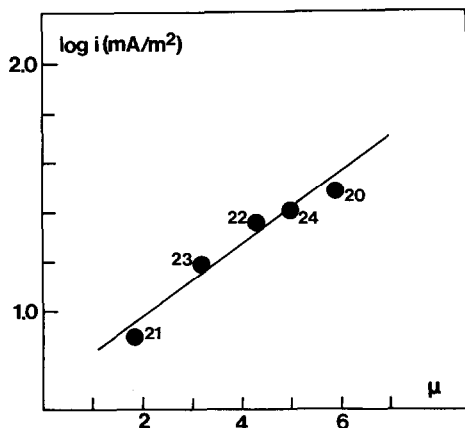


Fig. 4. The catalytic activity (measured as $\log i$ (mA m⁻²) at the electrode potential -20 mV vs. the Hg/HgO reference electrode) plotted against the magnetic moment of the oxides La(Mn,Cu)O₃. The numbers refer to Table 1.

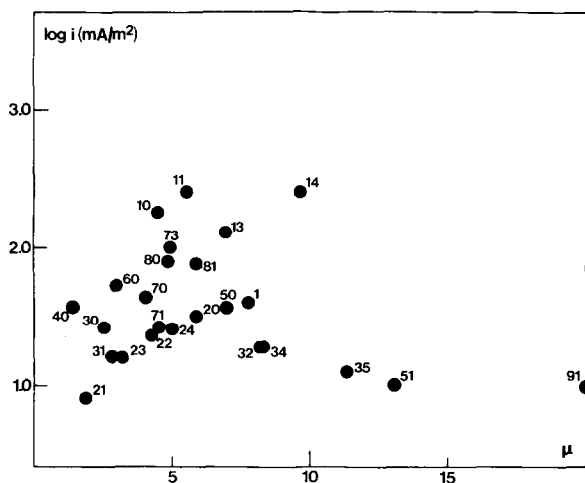


Fig. 5. The catalytic activity of all the investigated oxides. Activity is measured as given for Fig. 4. The point (1.60; 32) for La_{0.8}Pb_{0.2}MnO₃ is omitted to make the graph of reasonable size. It indicates a possible increase of activity for very high magnetic moments and thus constitutes a deviation from the 'Tseung effect' (cf. text) that can otherwise be traced for the non-paramagnetic systems.

The spread of points in Fig. 5 is not very encouraging. It is hard to find a convincing relation between the catalytic efficiency and the magnetism of the catalyst. Indeed, the graph looks very much the same as those that one finds in many treatises on catalysis in general. The lesson to be learned is probably that there is not a very pronounced correlation between the properties under discussion.

The data in Fig. 5 can be summarized so that there seems to be a least value of catalytic effect for such species where the magnetic moment is about 1.8 BM. This is close to the value for the magnetic moment of the superoxide ion, O_2^- , indicating the presence of only one unpaired electron in each molecule. It has been suggested [13, 14] that the rate determining step in alkaline media involves precisely the superoxide ion adsorbed (coordinated) at the surface



Our observation might therefore imply that the one-to-one electron arrangement gives an unfavourable interaction between reactant and catalyst and that the more unpaired electrons in the paramagnetic catalysts, the better will the reactant be ordered towards the reaction site. The decrease of catalytic effect towards the right hand side of the figure, when the formal magnetic moment of the systems get considerably above what is expected for a paramagnetic state, agrees qualitatively with the findings of Hibbert and Tseung [7].

Summing up, one might suggest that a purely magnetic influence on the electrocatalysis is not very pronounced. The several orders of magnitude variation in the current density has to be explained otherwise. It is, however, important to note that the weak influence that might be deduced is in agreement with previous analysis of the reaction mechanism.

Acknowledgements

This work is part of a project supported by the Swedish Research Council for Natural Sciences (NFR) and the Swedish Board for Technical Development (STU). The assistance of Ms Karin Trankèll, Ms Lena Timby and Ms Birgitta Svensson in carrying out the experiments is also acknowledged.

References

- 1 Y. Matsumoto, H. Yoneyama and H. Tamura, *Chem. Lett.*, (1975) 661.
- 2 D. B. Meadocroft, *Nature (London)*, 226 (1970) 847.
- 3 Y. Matsumoto, H. Yoneyama and H. Tamura, *J. Electroanal. Chem.*, 83 (1977) 237.
- 4 H. Tamura, H. Yoneyama and Y. Matsumoto, in S. Trassatti (ed.), *Electrodes of Conductive Metallic Oxides*, Elsevier, Amsterdam, 1980, Ch. 6.
- 5 J. B. Goodenough and J. M. Longo, *Crystallographic and Magnetic Properties of Perovskite and Perovskite Related Compounds*, Landolt Börnstein Tabellen, Neue Serie III/4a, Springer, Berlin, 1970.
- 6 F. S. Galasso, *Structure, Properties and Preparation of Perovskite-type compounds*, Pergamon, Oxford, 1969.
- 7 D. B. Hibbert and A. C. C. Tseung, *J. Electrochem. Soc.*, 125 (1978) 74.
- 8 M. Föex, A. Mancheron and M. Line, *C.R.*, 250 (1960) 3027.

- 9 L. A. Sazonov, Z. V. Moskvina and E. V. Artomonov, *Kinet. Katal.*, 15 (1974) 120.
- 10 J. Albertsson, Å. Oskarsson and K. Ståhl, *Acta Chem. Scand., Ser. A*, 36 (1982) 783.
- 11 L. Y. Johansson and R. Larsson, *J. Mol. Catal.*, 38 (1986) 61.
- 12 R. Haul and G. Dumbgen, *Chem.-Ing.-Tech.*, 32 (1960) 349.
- 13 D. Sawyer and E. Seo, *Inorg. Chem.*, 16 (1977) 499.
- 14 Z. W. Zhang, D. Tryk and E. Yeager, *Ext. Abstr., The Electrochem. Soc. Natl. Meet., Washington, DC, Oct. 1983*, Vol. 83-2, Abstr. 394.