

Short communication

Enhanced electrocatalytic activity of carbon-supported MnO_x/Ru catalysts for methanol oxidation in fuel cells

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Abstract

This investigation reports the possible use of carbon-supported manganese octahedral molecular sieves (OMS-2) for the electrooxidation of methanol. The effect of combining these materials with a commercially available 5%Ru-carbon sample is examined. The activity of the OMS-2 materials is evaluated with respect to other forms of manganese oxides such as pyrolusite and nsutite. The OMS-2 materials show a synergistic interaction with the 5%Ru-C as well as the pyrolusite materials that enhances their electrochemical activities effectively. These OMS-2 materials are not only cost-effective but also very electrochemically active.

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1. Introduction

The development of the direct methanol fuel cell (DMFC) has seen significant progress over the past few years, especially in relation to electrocatalysis, optimization of the electrocatalyst|membrane interface, catalyst loading, etc. There have been many studies on various kinds of oxides, mixed oxides, perovskite, noble metals (bulk as well as supported), etc. [1–3]. Platinum-ruthenium is the most commonly used binary anode catalyst. There is, however, growing evidence that ternary and quaternary alloys containing platinum-ruthenium together with osmium and iridium exhibit better activity towards methanol oxidation. Our earlier studies [4,5] have shown that Pt-Sn bimetallic catalysts supported on activated carbon improve the kinetics of carbon monoxide oxidation. The superior performance of binary catalysts has been explained with the help of two models: (i) a bifunctional model in which the oxophilic metal acts as a site

for H₂O adsorption and (ii) an electronic model in which the alloying element contributes to the d electron density. The bifunctional model suggests that effective catalysts should contain at least two types of surface elements, namely, those that bind methanol and activate its C–H bond and those that adsorb and activate water so that ‘OH’ groups are produced. According to the electronic model, CO poisoning of active Pt sites is caused by back bonding from Pt orbitals to the π* orbital of CO. In Pt–Ru binary alloys, there is reduction in the back bonding due to interaction of Ru orbitals with the Pt orbitals and hence CO becomes less strongly bonded. This results in a higher positive charge on the carbon and thereby makes it more susceptible to nucleophilic attack by water and hence assists the oxidation of CO to CO₂.

Carbon-supported Pt–WO_{3–x} electrodes have been reported to be more active than conventional Pt–C catalysts. It is believed [6] that multiple oxidation states of W, such as W(V) and W(VI), and an ability to form labile hydrogen atoms in HWO₃ may be responsible for the electrocatalytic activity. The increased electrocatalytic activity has been attributed to oxyhydroxide surface structures associated

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with proton insertion electrodes and an active hydroxylated surface.

Materials such as carbon, zeolites, etc. have been the most studied support-materials for the oxidation of methanol. With zeolites, the enhanced activity of the materials is attributed to the cage-like structures [7,8]. These substances allow effective methanol adsorption and later help in the oxidation of the adsorbed poisonous CO formed at the end of the reaction.

Mn(IV) oxides are of several types and are characterized by tunnels of varying dimensions analogous to zeolites. Unlike zeolites, which are built from silica and alumina tetrahedra, Mn(IV) oxides are built from $[\text{MnO}_6]$ octahedra. Depending upon how the octahedra are connected, the manganese oxides with monodirectional channel structures are todorokite (OMS-1, 3×3 channels), cryptomelane (OMS-2, 2×2 channels), pyrolusite (1×1 tunnels), ramsdellite (1×2 channels) and nsutite. The last mentioned has a ramsdellite–pyrolusite intergrowth structure. The oxides are used as oxidation catalysts, ion-exchange materials, sensors, etc. [9,10], and are also known to show good electrochemical properties under various conditions. At present, manganese oxides find extensive use in dry cells and primary batteries. Recently, we have shown that nickel-modified manganese oxide films, produced by thermal decomposition of the salts to form the oxide phase on a platinum strip, show good electrochemical activity towards the oxidation of methanol [11].

Manganese oxides are known to exhibit good proton–electron intercalation properties. In this study, we have attempted the possible use of manganese octahedral molecular sieves (OMS-2) for the electrooxidation of methanol. The effect of combining these materials with commercially available Ru-carbon has been studied.

2. Experimental

2.1. Catalyst synthesis

The active MnO_x samples (OMS-2) were synthesized by the oxidation of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with KMnO_4 in acidic medium. In a typical synthesis, 0.037 M KMnO_4 was added to hot MnSO_4 (0.052 M) containing 3 ml of concentrated HNO_3 , and refluxed for 24 h [12]. Similarly, the carbon-supported sample was synthesized by taking appropriate quantities of the salts for the in situ generation of the phase on the support material such that the ratio of OMS-2 phase:5% Ru-C was 1:1. For comparison of activity, a pyrolusite manganese oxide (P) was synthesized by the thermal decomposition of Mn(II)NO_3 at 200°C . An International Common sample, IC8 (nsutite form), supplied by the Electrochemical Society, Cleveland, OH, USA was also used.

2.2. Characterization

Chemical analysis of the OMS-2 samples was performed to determine the composition of MnO_{1+x} ; percentage of

MnO_2 was determined by the standard ferrous ammonium sulphate method, and percentage of Mn was determined by the EDTA method. The acid sites of the synthesized samples were determined by temperature programmed desorption (TPD), in which ammonia was used as the probe molecule in a continuous flow type reactor (see Fig. 1).

Fourier transform infra-red analyses of the samples were undertaken in the range $400\text{--}4000\text{ cm}^{-1}$ with a Shimadzu DR-8031 FTIR spectrometer. X-ray diffraction (XRD) analyses of the samples were performed with a Shimadzu labX-100 diffractometer to confirm the phase compositions. The thermal stability of the samples was determined with a NETZCH STA 409 PC thermogravimetric/differential scanning, calorimetry (TG/DSC) instrument, at a heating rate of $10^\circ\text{C min}^{-1}$. The surface areas of the samples were obtained by means of the BET method using a SMART SORB 91 surface-area analyser.

2.3. Electrode preparation

The electrodes were made as follows. First, 50 mg of sample was taken along with 3 ml of isopropyl alcohol in a mortar and pestle and mixed well for about 5 min. Next, three drops of Nafion solution were added and mixed to make a homogeneous mixture. The resulting ink was applied to a $3\text{ cm} \times 1\text{ cm}$ toray carbon paper to obtain a catalyst loading of 10 mg over 1 cm^2 active of surface area. This strip was then dried in an oven at 403 K for 1 h for later use in polarization studies.

2.4. Chemical activity

Active manganese dioxides undergo H^+ ion exchange when stirred with KI solution in an aprotic solvent such as dimethyl formamide (DMF). A proportionate amount of I_2 from I^- is liberated. The I_2 is then estimated by titration with sodium thiosulphate. The volume of thiosulphate, thus consumed, indirectly gives the H^+ ion exchangeability of the active MnO_2 . In the present investigation, therefore, the H^+ ion exchange capacity is determined in a DMF medium and is expressed as the volume of thiosulphate consumed. The amount of $\text{S}_2\text{O}_3^{2-}$ increases with increase in catalytic activity. The H^+ ion exchange capacity is directly related

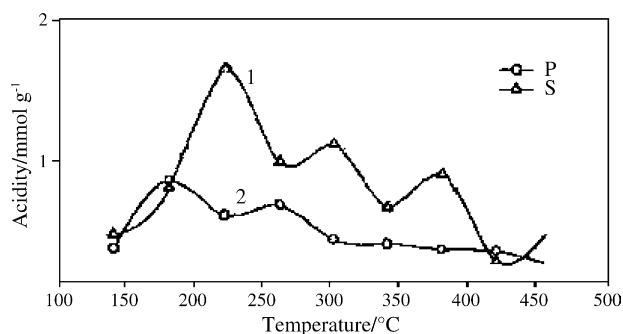
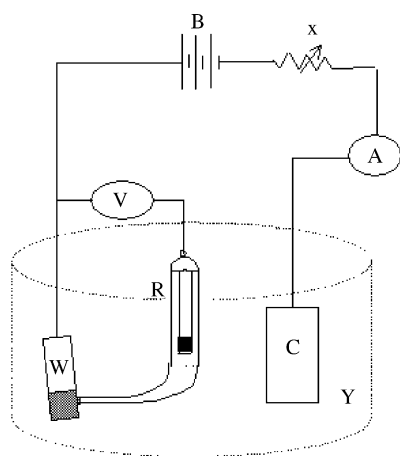


Fig. 1. Temperature programmed desorption of ammonia over OMS-2 catalysts S (curve 1) in relation to pyrolusite (curve 2).

to the presence of acidic 'OH' groups attached to Mn^{3+} in the host Mn(IV) oxide lattice. The catalytic activity should therefore depend on the presence of the active $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple.

2.5. Electrocatalytic activity

In the present investigation, electrochemical measurements were carried out in $2.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $1 \text{ mol dm}^{-3} \text{ CH}_3\text{OH}$ with a specially fabricated electrode described in Section 2.3 as the working electrode. Platinum foil was used as counter electrode, while a saturated calomel electrode (SCE) served as the reference electrode. The experimental set-up is shown in Fig. 2. The electrocatalytic activity is evaluated from the resulting Tafel plots.



B – Battery
X – Variable Resistance
A – Ammeter
V – Voltmeter
W – Working electrode
R – Reference Electrode
 (SCE with luggin capillary)
C – Counter Electrode (Pt foil)
Y – Cell containing $2.5\text{M H}_2\text{SO}_4 + 1\text{M MeOH}$

Fig. 2. Experimental set-up to study Tafel relationship.

3. Results and discussion

Chemical analysis of the OMS-2 samples reveals that the chemical composition was $\text{MnO}_{1.86}$ corresponding to average oxidation state of manganese of 3.72. This value is close to that reported by DeGuzman et al. [12] for materials obtained using different precursors. By comparison, the pyrolusite sample prepared by thermal decomposition of Mn(II) nitrate has a stoichiometric composition of MnO_2 wherein the oxidation state of manganese is +4.

The d and I/I_o and the lattice parameters are calculated from the XRD patterns on the basis of tetragonal unit cell given in Table 1. These are in agreement with the literature values [13] and also compare well with the JCPDS file 20-908 for cryptomelane $\text{KMn}_8\text{O}_{16}$. The peak at $d \approx 1.80 \text{ \AA}$ is a characteristic of cryptomelane OMS-2. The FTIR profiles of the samples also show OMS-2 characteristic bands at about 700 cm^{-1} . The prominent absorption peak at 700 cm^{-1} is generally not seen in pyrolusite and nsutite forms of manganese oxides [14].

The activity of the samples is given in Table 2, in relation to their other physicochemical characteristics, viz., surface area, O_2 loss by thermogravimetric analysis, acidity levels and volumes of thiosulfate (as a measure of H^+ ion exchange capacity of the OMS-2). The electrocatalytic activity of the samples is expressed in terms of i_{150} (current produced at an overpotential of 150 mV) as calculated from Tafel Plots (Figs. 3 and 4). These values are given in Tables 2 and 3.

It is seen from the data in Table 2 that the OMS-2 sample S produces a large current of 3.2 mA cm^{-2} . By comparison, the corresponding current given by the pyrolusite sample P is negligible. The poor activity of P is due to its stoichiometric nature and absence of any acidic OH groups. The high activity of S could be due to presence of labile oxygen and acidic OH groups, as discussed below.

It is known that the oxidation of alcohols on Mn(IV) oxides follow the Mars–van-Krevelen mechanism that involves participation of lattice oxygen [9,15]. In such a case, it can be hypothesized that the higher activity is associated with the extent of participation of lattice oxygen. In order to confirm this hypothesis, TG/DSC studies were conducted. Mn(IV)

Table 1
 X-ray diffraction data of OMS-2 catalyst

S		JCPDS 20-908		Ref. [13]	
d	I/I_o	d	I/I_o	d	I/I_o
6.7786	84	6.9	90	9.93	s
4.8572	68	4.9	80	4.90	vs
3.1186	94	3.1	80	3.1	vvs
2.3811	100	2.39	100	2.39	vvs
2.1373	39	2.25	60	2.14	s
1.8227	35	1.80	40	1.83	s
1.6274	35	1.63	60	1.63	w
1.5406	45	1.54	60	1.54	w
1.4210	–	1.35	50	1.42	w
$a = b = 9.7584 \text{ \AA}, c = 2.8463 \text{ \AA}$		$a = b = 9.84 \text{ \AA}, c = 2.86 \text{ \AA}$		$a = b = 9.81 \text{ \AA}, c = 2.85 \text{ \AA}$	

Table 2

Activity of Mn(IV) oxides in relation to their physicochemical characteristics (electrocatalytic activity expressed in terms of current produced at overpotential of 150 mV)

Catalyst	'x' in MnO _x	Crystal phase	BET (m ² g ⁻¹)	Thermal analysis			Acidity (mmol g ⁻¹)	VS ₂ O ₃ ²⁻ (ml)	i ₁₅₀ (mA cm ⁻²)	
				% O ₂ loss						
				120–300 (°C)	300–500 (°C)	500–570 (°C)				
S	1.86	Cryptomelane (OMS-2)	77	4.45	4.44	2.4	600	1.66	3.3	3.2
P	2	Pyrolusite	7	2.8	3.29	1.2	597	0.78	0	0.3

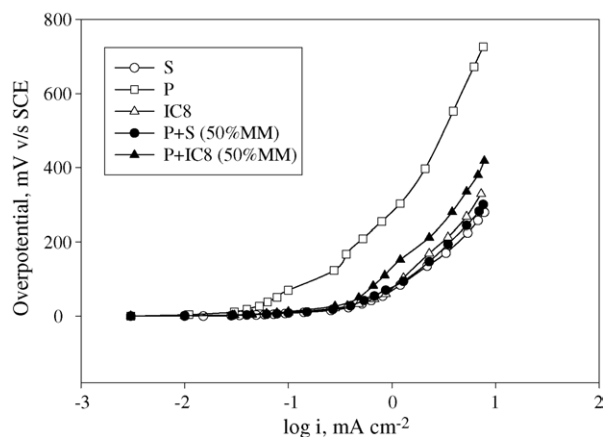


Fig. 3. Tafel plots to study effect of pyrolusite (P) on OMS-2 (S) and nsutite (IC8).

oxides are known to lose progressively: (i) bound water and some physisorbed oxygen up to 300 °C [16]; (ii) chemisorbed oxygen and some lattice oxygen up to about 500 °C; (iii) oxygen beyond 500 °C until the decomposition temperature is more reflective of only lattice oxygen loss [14,16]. At around 600 °C, thermal decomposition of the type MnO₂ → Mn₂O₃ occurs [14]. In the present case, this decomposition occurs at about 600 °C. The various TG weight losses in the temperature range 120–570 °C are given in Table 2. Beyond this temperature the OMS-2 structure will not be stable. The weight loss between 500 and 570 °C will be pure loss of lattice

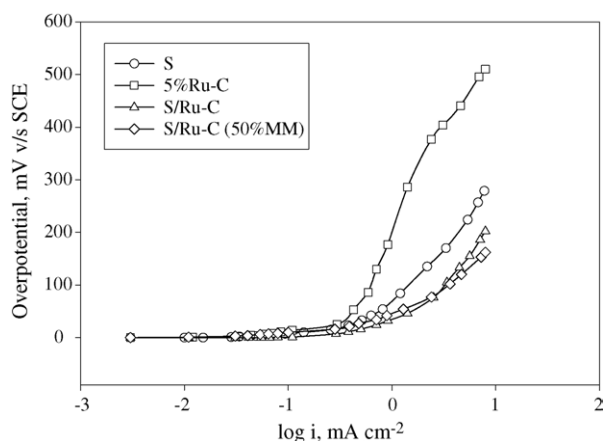
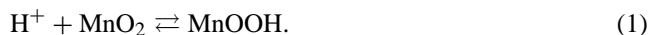


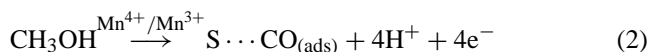
Fig. 4. Tafel plots of OMS-2 (S), 5%Ru-C and their mixtures.

oxygen. The active OMS-2 sample shows greater oxygen loss in all the three temperature intervals. Therefore, the catalytic activity can be directly related to the rate of oxygen evolution as evident from the TG and presence of acidic 'OH' groups attached to Mn³⁺ in the host Mn(IV) oxide lattice.

It is also evident from the data in Table 2 that the H⁺ ion exchange capacity, expressed as volume of thiosulfate consumed VS₂O₃²⁻, increases with increase in catalytic activity. The H⁺ ion exchange capacity depends on the MnOOH group. The mobile H⁺ ions can then hop on to neighboring Mn⁴⁺ sites to generate new Mn³⁺, i.e.,



The activity may therefore be related directly to the presence of the active Mn⁴⁺/Mn³⁺ redox couple, which may be responsible for the acid centres in the catalysts as evident in the TPD data. Suib and co-workers [15] have in fact suggested the presence of such strong Lewis acid centres. It is further seen from Table 2 that the OMS-2 sample has stronger acid sites than the pyrolusite sample. Hence, the electrocatalytic oxidation of methanol may be mediated by (i) lattice oxygen and (ii) the Mn⁴⁺/Mn³⁺ redox couple. It is believed that methanol dehydrogenation is catalyzed by the Mn⁴⁺/Mn³⁺ redox couple by the evolution of protons and electrons, i.e.,



followed by oxidation of the residual CO-type species by lattice oxygen. The resulting anion vacancy would be healed by absorption of dissolved oxygen into the OMS-2 lattice,

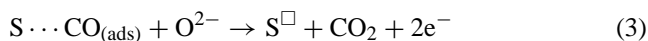
Table 3

Electrocatalytic activity of samples expressed in terms of current produced at arbitrarily chosen overpotential of 150 mV

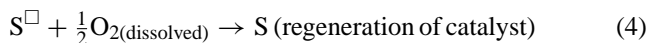
Sample	i ₁₅₀ (mA cm ⁻²)
S	3.2
P	0.3
IC8	2
P/S	2.8
P/IC8	1.2
5%Ru-C	0.75
S/Ru-C	5.6
S/Ru-C (50% MM) ^a	7.2

^a 50% MM: mechanical mixture containing 50% OMS-2 compound.

according to:

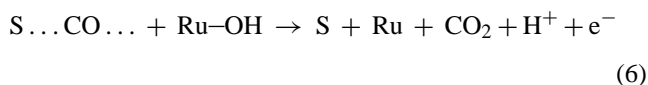
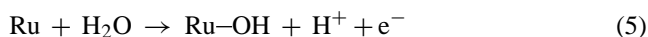


where \square is lattice vacancy.



Further investigations carried out on the International sample, IC8, resulted in high currents although the OMS-2 sample was still superior. To understand the effect of pyrolusite, mechanical mixtures of pyrolusite and nsutite were prepared in a 1:1 ratio and subjected to activity tests. As can be seen from Table 3, the pyrolusite/IC8 mixture does not increase the activity in terms of the current produced. On the other hand, the current produced by the pyrolusite/OMS-2 mixture produces almost the same current as pure OMS-2 ($\sim 3.0 \text{ mA cm}^{-2}$). This demonstrates that even though pyrolusite is itself inactive, it gives the same result as OMS-2 with 50% reduction in the OMS-2 quantity in the final electrode mixture. Thus, pyrolusite produces a synergistic interaction with OMS-2 but not with nsutite.

It is well known that Ru in Pt-Ru alloy catalysts greatly enhances the electrocatalytic activity of Pt. In order to study the effects of Ru on OMS-2, further investigations were carried out with a commercially available 5%Ru-C sample (supplied by Arora Matthey Co. Ltd., Calcutta, India). Activity tests were carried out by synthesizing 50% OMS-2 on 5%Ru-C and also by preparing electrodes by 1:1 mechanical mixing of separately prepared OMS-2 with 5%Ru-C. The results are also presented in Table 3. It is seen that the commercial 5%Ru-C used in the present investigation displays a much lower activity compared with the MnO_x materials OMS-2 or IC8. The current on 5%Ru-C is only 0.75 mA cm^{-2} . On the other hand, OMS-2/Ru-C electrodes give a large increase in current. The electrode prepared from 1:1 mechanical mixture produces a synergistic interaction and delivers a current of 7.2 mA cm^{-2} . Thus, it is even superior to the OMS-2/Ru-C in situ prepared sample. The mechanism is given by:



It is believed that Ru provides nucleating centres for CO clustering within the octahedral sieve framework of OMS-2 as in case of zeolite structures [7] and this causes facile oxidation of CO to CO_2 .

4. Conclusions

The following conclusions can be drawn from the above study.

- (i) Manganese octahedral molecular sieves have been successfully synthesized and found to be active for methanol electrooxidation.
- (ii) The high activity of manganese oxide is associated with the presence of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple and the extent of participation of lattice oxygen plays an important role in methanol oxidation.
- (iii) Pyrolusite in combination with manganese octahedral molecular sieves gives a higher current (more than twice) than that produced by a combination of pyrolusite with the international sample (IC8). This suggests that it produces a synergistic interaction with OMS-2 and thus improves its activity towards methanol oxidation.
- (iv) In case of OMS-2 materials in combination with 5%Ru-C (whether an in situ generated phase on the Ru-C or a 1:1 mechanical mixture), Ru acts as nucleating centres for CO clustering within the octahedral sieve framework of OMS-2 and promotes, facile oxidation of CO to CO_2 .

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References

- [1] S. Wasmus, W. Vielstich, *J. Appl. Electrochem.* 23 (1993) 120.
- [2] R. Ramkumar, S. Dheenadayalan, R. Patabiraman, *J. Power Sources* 69 (1997) 75.
- [3] A.S. Arico, et al., *Electrochim. Acta* 39 (1994) 691–700.
- [4] A.E. Aksoylu, M.M.A. Freitas, J.L. Figueiredo, *Appl. Catal. A: Gen.* 192 (2000) 29–42.
- [5] A.E. Aksoylu, M.M.A. Freitas, J.L. Figueiredo, *Catal. Today* 62 (2000) 337.
- [6] A.K. Shukla, M.K. Ravikumar, A.S. Arico, G. Candiano, V. Antonucci, N. Giordano, A. Hamnett, *J. Appl. Electrochem.* 25 (1995) 528.
- [7] P.V. Samant, J.B. Fernandes, *J. Power Sources* 125 (2004) 172–177.
- [8] S. Surampudi, A. Frank, R. Narayanan, W. Chun, B. Jeffries-Nakamura, A. Kindler, G. Halpert, U.S. Patent No. 2, 001,005,0230 (December 13, 2001).
- [9] J.S. Rebello, J.B. Fernandes, *Indian J. Chem A* 43A (2004) 1676–1679.
- [10] S.L. Suib, *Chem. Innov.* 30 (2000) 27.
- [11] P.V. Samant, J.B. Fernandes, *J. Power Sources* 79 (1999) 114.
- [12] R.N. DeGuzman, Y.F. Shen, E.J. Neth, S.L. Suib, C.L. O'Young, S. Levine, J.M. Newsam, *Chem. Mater.* 6 (1994) 815.
- [13] K.M. Parida, S.B. Kanungo, B.R. Sant, *Electrochim. Acta* 26 (1981) 435.
- [14] J.B. Fernandes, B.D. Desai, V.N. Kamat Dalal, *J. Appl. Electrochem.* 15 (1985) 351.
- [15] V.D. Makwana, Y.C. Son, A.R. Howell, S.L. Suib, *J. Catal.* 210 (2002) 46.
- [16] X. Chen, Y.F. Shen, S.L. Suib, C.L. O'Young, *Chem. Mater.* 14 (2002) 940.