

Can $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ be used as anodes for direct methanol fuel cells?[☆]

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Abstract

Attempt has been made to obtain the relationship between the electrophysical and electrochemical properties in order to provide a possible basis for designing new electrode materials for fuel cell applications. The substituted lanthanum cuprates of composition $\text{La}_{2-x}\text{M}_x\text{Cu}_{1-y}\text{M}'_y\text{O}_4$ (where M = Sr, Ca and Ba; M' = Sb and Ru; $0.0 \leq x \leq 0.4$ and $y = 0.1$) were used to demonstrate the correlation of the Fermi level and carrier concentration with the methanol oxidation onset potential and activity, respectively. The activity of bulk material is compared with that of the nanocrystalline material prepared by the polymer modified sol–gel method. The nanocrystalline material was characterized by TGA, XRD, SEM, TEM and cyclic voltammetry. © 2002 Published by Elsevier Science Ltd.

Keywords: Direct methanol fuel cells; Perovskite; Anode electrocatalyst

1. Introduction

The search for less expensive alternate materials as anodes for direct methanol fuel cells (DMFC) has been a topic of interest. Conventionally, noble metals such as Pt and Pt–Ru bimetallic systems have been employed as electrocatalysts for methanol oxidation in acid and alkaline media [1,2]. Noble metal sites are known to be poisoned by the methanol oxidation intermediates, such as CO species, formed during the oxidation reaction. This accounts for the experimentally observed deterioration in the performance of noble-metal based fuel cell electrodes. Several ambient temperature DMFC have been reported employing dispersed platinum-based electrocatalysts in polymer electrolyte (Nafion 117) [3,4]. The applicability of Pt-based electrodes is restricted because of the accumulation of surface poisoning intermediates, thus leading to loss of activity with time. One way of avoiding poisoning is to alloy the platinum with oxophilic metals such as Ru and Sn. Another approach to avoid such poisoning phenomenon is to employ electronically conducting mixed oxides as anode materials. Though various attempts have been made earlier to use oxides of V, Fe, Ni, In, Sn, La and Pb [5], non-noble metallic glasses [6] and carbides [7], none of these has shown any measurable activity for methanol oxidation

except the carbides. The major problem associated with metallic glasses seems to be the electrode stability during operating conditions. In recent years, studies on various transition metal mixed oxides have shown the applicability of perovskite oxides as substitutes for noble metals as fuel cell electrodes at high temperatures 900–1000 °C [8–13]. Moreover, perovskite oxides have prospects for elucidating the correlation between the electrophysical property of the electrode surface and electrocatalysis.

Electrodes, normally considered as source and sinks for electrons, have to perform various other functions as well for effective charge transfer at the electrode/electrolyte interface. The differences in the magnitude of conductivity between an oxide (semiconductor) and metal electrodes are predominantly reflected in the concentration of the free charge carriers. A diffuse space charge (Garrett–Brattain) exists inside the bulk of the solid, apart from the Helmholtz and Gouy–Chapman layer and as a result a potential gradient develops inside the bulk of solid electrode (field penetration) [14,15]. Therefore, any electron in the space charge region will interact with the field, and its Fermi energy (electrochemical potential of the electron) will either increase or decrease compared with the value in the absence of the field. The charge transfer process across the interface will occur only when the Fermi level of the electrode is located close to the redox potential (E_{redox}^0) of the depolarizer. The charge transfer rate in the non-equilibrium condition depends on the surface concentration of the charge carriers. The position of the Fermi level determines

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the chemisorption properties on the surface, and controls the equilibrium population of the various species. To examine the multicomponent systems for electrode applications, the characteristics one has to consider are

1. The system should have sufficient electronic conductivity.
2. The system should possess considerable density of states so as to give requisite field penetration.
3. The system should be amenable for alteration of the Fermi level by suitable substitutions at both cationic and anionic positions.

On the basis of the considerations given above, one has a limited number of mixed oxide systems like perovskites, spinels and to some extent pyrochlores, which satisfy these necessary conditions. Since redox reactions are normally controlled by the redox potentials of the depolarizer in the electrolyte medium, an inherent possibility of altering the valence and conduction band positions of the semiconductors are an added advantage since these in situ alterations can be utilized for an effective redox process.

The extent of in situ alteration of valence and conduction band edges of the semiconductor by the depolarizer (methanol) depends on the extent of the interaction of the H^+ or OH^- , depending on the pH of the electrolyte, with the semiconductor. Therefore, for choosing a proper semiconducting oxide as electrode for methanol oxidation, the important point to be considered is the weak interaction of oxide with the H^+ or OH^- ions so that in situ alterations of the band edges of the semiconductor by the depolarizer can be effectively utilized. In the case of transition metal containing perovskites, the M^z-OH bond strength depends on the number of electrons occupying the antibonding orbitals of M^z-OH . The M^z-OH bond strength is weak in the case of copper containing perovskites [12].

Recently, we have examined the electrocatalytic properties of substituted perovskite of compositions $La_{2-x}M_xCu_{1-y}M'_yO_4$ (where $M = Sr, Ca$ and Ba ; $M' = Sb$ and Ru ; $0.0 \leq x \leq 0.4$ and $y = 0.1$), prepared by conventional ceramic method, for methanol oxidation in alkaline medium [16]. Perovskites of composition A_2BO_4 incorporating rare and alkaline earth cations in their A lattice sites and the cation substituents into the B lattice sites have great influence over electrocatalytic activity and onset potential for electrochemical oxidation of methanol. The crystal structure of perovskite of composition A_2BO_4 is shown in Fig. 1. The activity of these electrodes for methanol oxidation is lower for these oxides compared to that obtained for Pt, but the electrode tolerance towards oxidation intermediates was found to be better than that of unsupported (bulk) as well as supported, Pt systems. These oxides, when fabricated in nanocrystalline form, can be expected to exhibit altered electrochemical behavior by virtue of an enhanced surface to volume factor as well as due to alterations in the density of states by introducing

Schokley states in the diffuse space charge region inside the solid.

In the present study, the influence of Fermi level and carrier concentration on the methanol oxidation onset potential and activity, respectively, is reported. The activity of bulk material is also compared with that of the nanocrystalline material prepared by the polymer modified sol–gel method. The nanocrystalline material was characterized by TGA, XRD, SEM, TEM and cyclic voltammetry.

2. Experimental

2.1. Preparation of nanocrystalline $La_{1.8}Sr_{0.2}CuO_4$

The chemicals used for the synthesis of nanocrystalline lanthanum strontium copper oxide of composition $La_{1.8}Sr_{0.2}CuO_4$ are Lanthanum nitrate (CDH, 99.1%), strontium nitrate (s.d.fine chemicals Ltd, 99%) and copper nitrate (s.d.fine chemicals Ltd, 99%). Polyacrylamide gel was used as protecting agent to prevent crystal growth. High molecular weight polyacrylamide was prepared by radical polymerization using H_2O_2 as radical generator [17].

The polyacrylamide gel solution was prepared by adding 2 g of polyacrylamide gel to 500 ml distilled water and the resulting solution was kept for 2 days to obtain sufficient viscosity. The concentration of the polymer gel solution was 0.4%. The desired stoichiometric amounts of metal nitrates were taken in one burette and in another burette 5% KOH solution was taken. The solutions from the two burettes were added with vigorous stirring into the gel solution maintained at 75–80 °C. The flow rates from the burettes were adjusted in such a way that the pH of the gel solution was maintained at 7.5–8.0. After the completion of precipitation, the precipitate was aged for 30 min at 75–80 °C, followed by filtration and then it was dried in an air oven maintained at 100 °C. The precursor was calcined at 500 °C for 3 h in air.

2.2. Characterization methods

The thermal analyses were obtained using a Perkin–Elmer TGA-7, heating up to 800 °C in an air atmosphere at the scan rate of 20 °C/min. XRD analyses were carried out on a Rigaku miniflex instrument using Fe-filtered $Co K\alpha$ ($\lambda = 1.7902 \text{ \AA}$) radiation (35 kV, 25 mA) at room temperature. The CHN analyses were carried out using a Heraeus Elemental Analyser Model CHN-O rapid analyzer. The SEM and TEM measurements were carried out using a JEOL 1500 Scanning Microscope and a Philips CM12/STEM, Scientific and Analytical Equipment.

2.3. Electrochemical studies

The electrochemical oxidation of methanol was carried out using cyclic voltammetry (Potentiostat Wenking Model POS 73). The reference and counter electrodes used in the

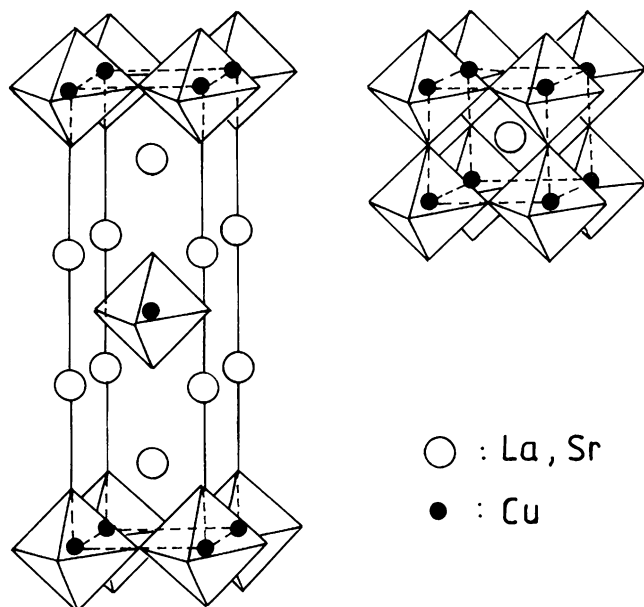


Fig. 1. Perovskite A_2BO_4 electrocatalyst crystal structure. Oxygen ions are at the points of the octahedral.

present work were saturated Ag/AgCl and Pt foil (1.5 cm^2), respectively. The methanol oxidation was carried out in 1 M KOH and 1 M CH_3OH .

The electrode was fabricated as follows: 20 mg of oxide was dispersed in 0.5 ml distilled water and ultrasonicated for 30 min. From the dispersion, 20 μl of dispersion were placed on to a glassy carbon disk (ϕ 2 mm diameter), which was previously polished with alumina followed by ultrasonication for 2 min, and dried in air, which was followed by the addition of 5 μl of 5% Nafion solution as binder.

3. Results and discussion

3.1. Characterization of nanocrystalline cuprate

The TGA obtained for polyacrylamide gel, precursor oxide without polyacrylamide and precursor oxide/polyacrylamide matrix is shown in Fig. 2. The peak at 110°C corresponds to the removal of physisorbed water from the gel. The decomposition of polymer takes place at 465°C . The peak at 300°C corresponds to the water removal during the condensation process to form the oxide framework. The condensation peak is narrow in the presence of polymer (Fig. 2(c)) compared to that in the absence of polymer (Fig. 2(b)). This may be due to the sufficient thermal conductivity provided by the polymer to complete the condensation process in lower temperature range.

To optimize the calcination temperature and time, the precursor was calcined at different temperatures and also by varying the time at constant temperature. The particle size was calculated from full width at half maximum from the X-ray diffraction pattern using the Debye-Scherrer equation

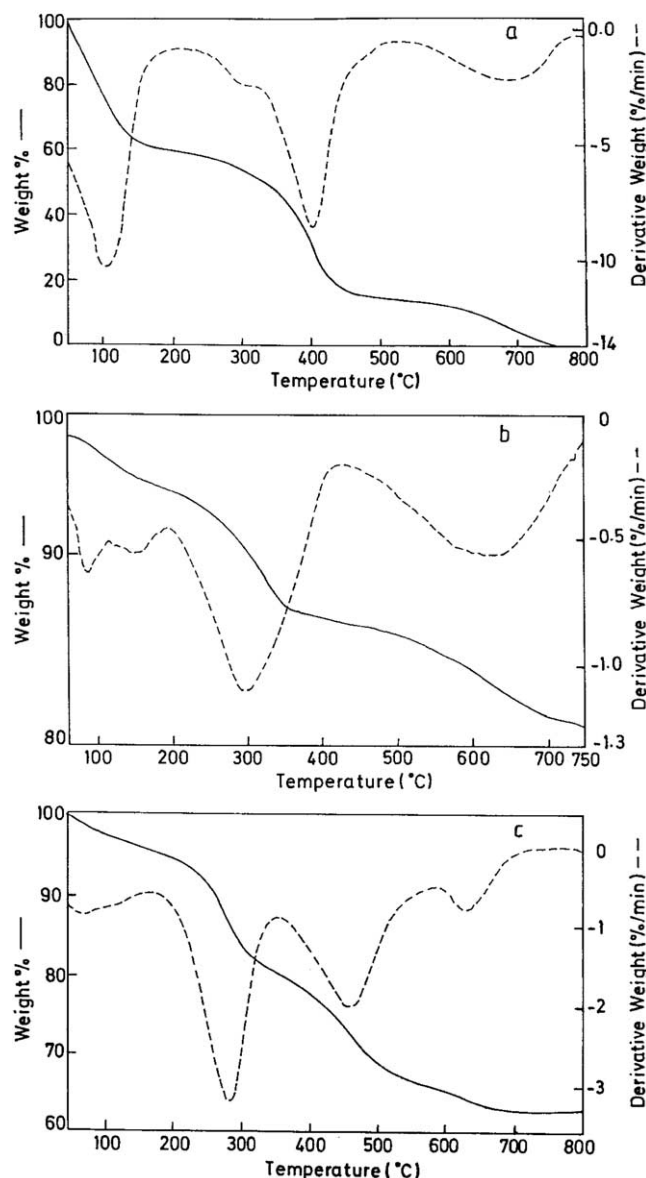


Fig. 2. Thermogram obtained for (a) polyacrylamide gel, (b) oxide precursor without polyacrylamide and (c) oxide/polyacrylamide composite in air atmosphere.

and is given in Table 1. The optimized calcination temperature and time is 500°C for 3 h.

The X-ray diffraction pattern obtained for the lanthanum cuprate of composition $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ prepared by the polymer modified sol-gel method is shown in Fig. 3, which confirms the single phase oxide formation (JCPDS standard file No. 38-1427). The XRD peaks are characteristically broader than normally obtained for large crystallites, which is expected for nanosized crystallites.

The percentage of C (1.5%), H (0.3%) and N (nil) in the calcined material was very low, which confirms the complete removal of the polymer.

It is seen from the SEM pictures (Fig. 4) that the material prepared by a solid state method (Fig. 4(a)) shows higher agglomerate size with broad particle size distribution

Table 1
Effect of calcination temperature and time on crystallite size

Calcination temperature (°C)	Calcination time (h)	Crystallite size (nm)
600	12	24
500	3	6
450	12	10.7
450	24	12
450	36	12
450	48	12

whereas a fine distribution of oxide particles was achieved using the polymer modified sol–gel method (Fig. 4(b)).

Fig. 5 shows the TEM pictures of the oxide, taken in different regions of the sample prepared by the polymer modified sol–gel method. It is seen from the TEM pictures that the overall particle size of the lanthanum cuprate oxide ranges from 1 to 14 nm and that particles exhibit fine spherical features.

3.2. Electrochemical studies of bulk and nanocrystalline cuprate

The substituted rare earth cuprate of composition $\text{La}_{2-x}\text{M}_x\text{Cu}_{1-y}\text{M}'_y\text{O}_4$ (where $\text{M} = \text{Sr}, \text{Ca}$ and Ba ; $\text{M}' = \text{Sb}$ and Ru ; $0.0 \leq x \leq 0.4$ and $y = 0.1$) crystallized in single phase was examined as electrodes (in disk type) for oxidation of methanol. The oxidation onset potential is high compared to that of platinum. The active site for methanol oxidation is deduced to be $\text{Cu}(3+)$ ions. The details of the study leading to these conclusions are reported elsewhere [16,18]. In semiconductor electrodes, considerable electron transfer across the interface can occur only when the redox potential of the depolarizer (methanol) is close to the Fermi level of a semiconductor. The magnitude of overpotential required for oxidizing methanol depends on the position of the Fermi level in the band gap of the oxide electrode with respect to the redox potential of the methanol. The Fermi energy was calculated for the substituted rare earth cuprate from the redox potential obtained from the cyclic voltammogram in the absence of methanol using the relation [19–21]

$$E_F = -(4.5 \text{ eV} + eU_{\text{redox}}),$$

and is shown in Fig. 6. It is seen from Fig. 6 that, for an effective charge transfer process (oxidation) to occur the

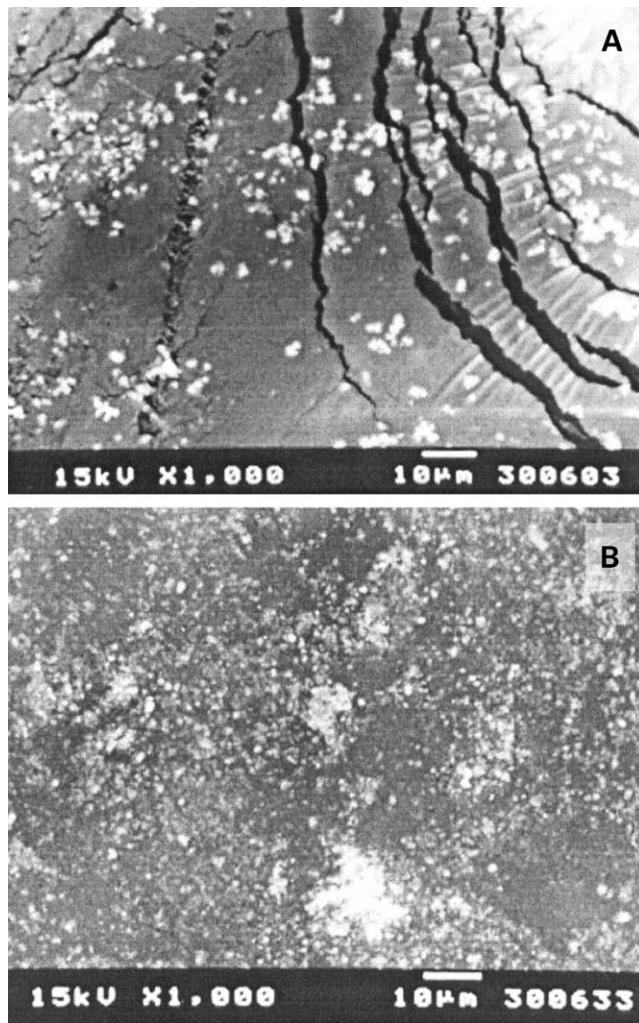


Fig. 4. Scanning electron micrographs of $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ prepared by (A) conventional ceramic method and (B) polymer modified sol–gel method.

reduction potential of the electrode should be higher than that of the redox potential of the methanol. The overpotential that is applied is to bring the reduction potential of the electrode higher than that of the redox potential of the methanol. Therefore, the magnitude of the overpotential depends on the difference between the reduction potential of the electrode and the redox potential of the methanol

$$\eta = (E_{\text{electrode}} - E_{\text{methanol}}).$$

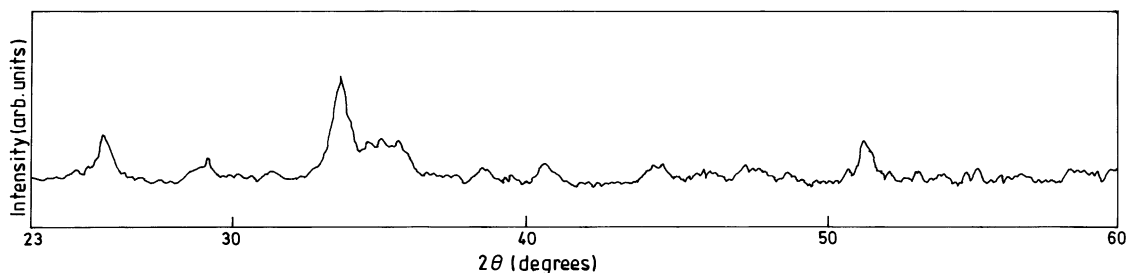


Fig. 3. X-ray diffraction pattern obtained for nanocrystalline $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$.

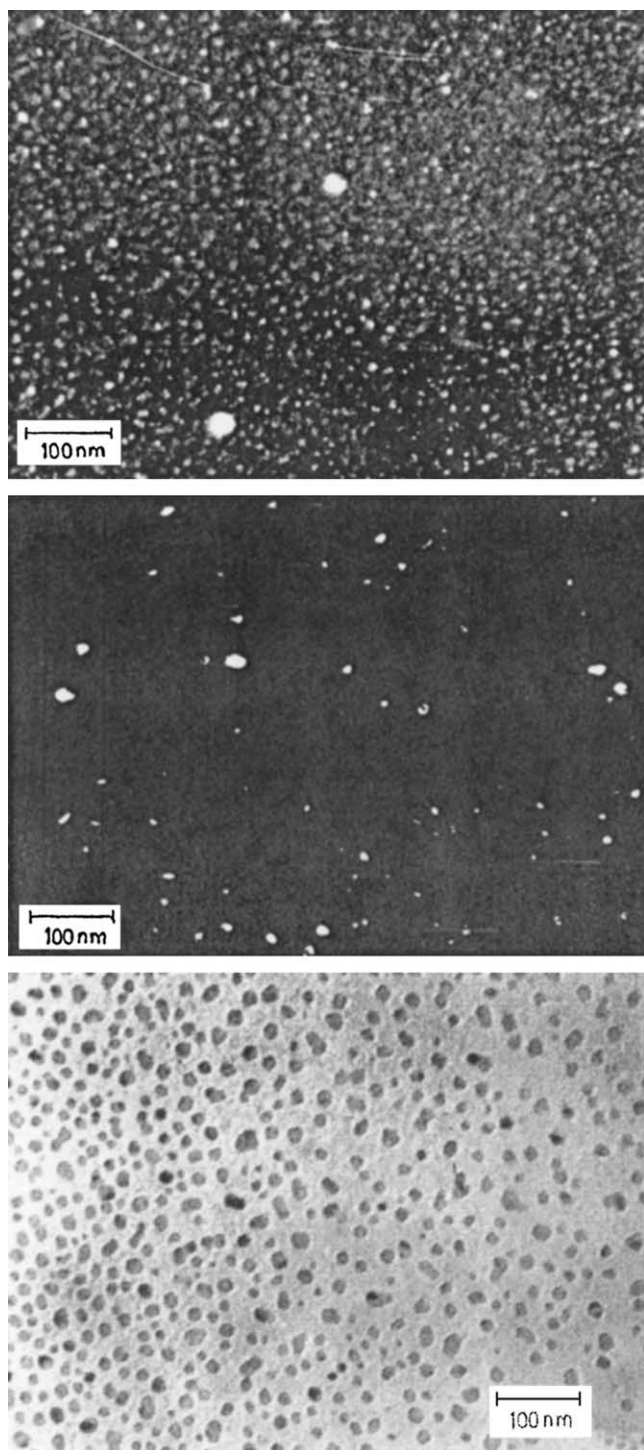


Fig. 5. Transmission electron micrographs of $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ taken in different region (particle size ranges 1–14 nm).

The variation in the Sr content does not influence the reduction potential or E_F of the electrode significantly. The substitution at A sub-lattice by Ca and Ba alters the reduction potential of the electrode to more negative values. Thus high overpotentials are required. The substitution of Sb and Ru at B lattice shifts the reduction potential of the electrode more positive and

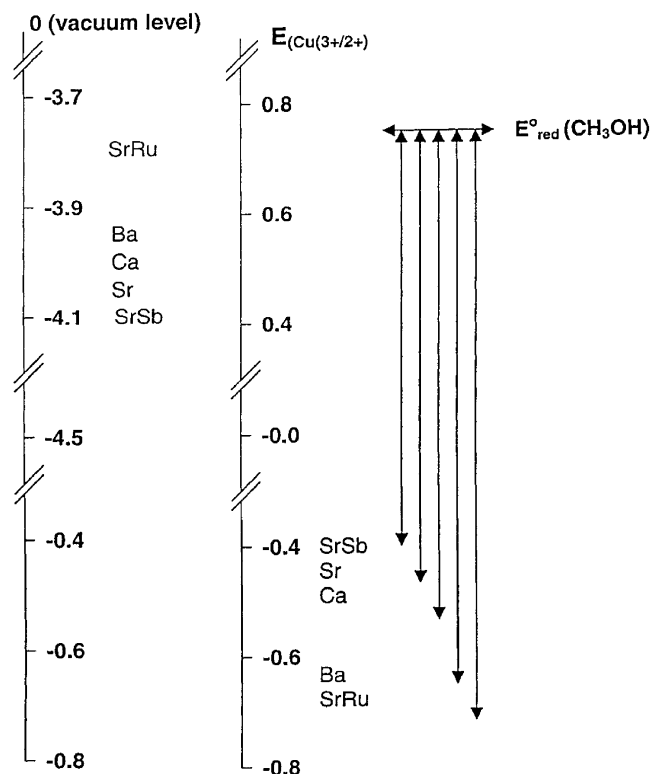


Fig. 6. Correlation between the Fermi level of the electrode with methanol oxidation onset potential.

negative value with respect to the unsubstituted B composition, respectively, hence low and high overpotentials are required for Sb and Ru substituted systems, respectively. Thus, the methanol oxidation onset potential follows the order

$$\text{SrSb}(0.34 \text{ V}) < \text{Sr}(0.46 \text{ V}) < \text{Ca}(0.51 \text{ V}) < \text{SrRu}(0.76 \text{ V}) < \text{Ba}(0.78 \text{ V}).$$

The numbers in the brackets represent the methanol oxidation onset potential. Thus the methanol oxidation onset potential depends on the position of the Fermi energy or redox potential of the electrode with respect to the redox potential of the depolarizer (methanol).

Certain electrophysical characteristics and the electrochemical activities of substituted cuprates for methanol oxidation are given in Table 2. On altering the Sr content as well as the nature of alkaline earth metal at the A sub-lattice, variations in the electrical conductivity, carrier concentration (or density of states) and the electrochemical activity for oxidation were observed. The change in activity was found to have a good correlation with the carrier concentration (refer to Table 1). The maximum activity was observed for the composition where the carrier concentration is at a maximum. Since it is known that the activity depends on the rate of charge transfer reaction (current density) across the electrode/electrolyte interface, this in turn, depends on the density of states.

Table 2
Electrophysical and electrochemical characteristics of substituted lanthanum cuprates

Electrocatalyst ^a	Cu(2 +) ^b	Cu(3 +) ^b	Hole concentration (cm ⁻³)	Activity ^c <i>I</i> (mA/cm ²)
La _{1.9} Sr _{0.1} CuO ₄	0.921	0.079	1.99×10^{20}	8.0
La _{1.8} Sr _{0.2} CuO ₄	0.856	0.144	3.69×10^{20}	14
La _{1.7} Sr _{0.3} CuO ₄	0.938	0.062	1.89×10^{20}	0.6
La _{1.6} Sr _{0.4} CuO ₄	0.975	0.026	6.75×10^{19}	0.5
La _{1.9} Ca _{0.1} CuO ₄	0.965	0.035	8.76×10^{19}	3.3
La _{1.9} Ba _{0.1} CuO ₄	0.972	0.098	2.40×10^{20}	1.8

^a Prepared by conventional ceramic method.

^b Determined iodometrically [14].

^c At +0.6 V versus Hg/HgO.

The dependence of the density of states of the electrode (oxide) on the rate of charge transfer reaction of the depolarizer [19,22] follows the equation given below:

$$I = k_{c+}N_cN_{\text{red}} - k_{c-}n_sN_{\text{ox}},$$

$$n_s = n_0 \exp(e_0jDSC/kT),$$

where n_s is surface concentration of electrons/holes.

These oxides, when fabricated in nanocrystalline form, can be expected to exhibit altered electrochemical behavior by virtue of enhanced surface to volume factor as well as

due to alterations in the density of states by introducing surface states in the diffuse space charge region inside the solid [23]. The maximum activity for methanol oxidation is exhibited by the composition La_{1.8}Sr_{0.2}CuO₄ and hence this composition was chosen for the preparation in nanocrystalline form.

Typical cyclic voltammogram obtained for the strontium substituted rare earth cuprate of composition La_{1.8}Sr_{0.2}CuO₄ (ceramic method) as the electrode in 1 M KOH is shown in Fig. 7(a). The anodic currents obtained at potentials greater than 0.7 V versus Ag/AgCl is due to the oxygen evolution reaction. Fig. 7(b) shows the cyclic voltammogram obtained for the oxidation of methanol. It is seen that the methanol oxidation onset potential is at +0.48 V. Fig. 8 shows the cyclic voltammogram obtained for the oxidation of methanol using nanocrystalline La_{1.8}Sr_{0.2}CuO₄. The methanol oxidation onset potential is 0.4 V. The activity (measured at +0.6 V versus Ag/AgCl) is three times higher when nanocrystalline oxide is used as anode compared to that of the oxide prepared by solid-state method (refer to Table 3). Therefore, on decreasing the particle size, the activity is not only enhanced but there is a shift of methanol oxidation onset potential towards the cathodic side by 0.08 V.

The enhanced activity observed for the nanocrystalline lanthanum cuprate compared to that of the bulk oxide may be due to the high density of surface states in the space

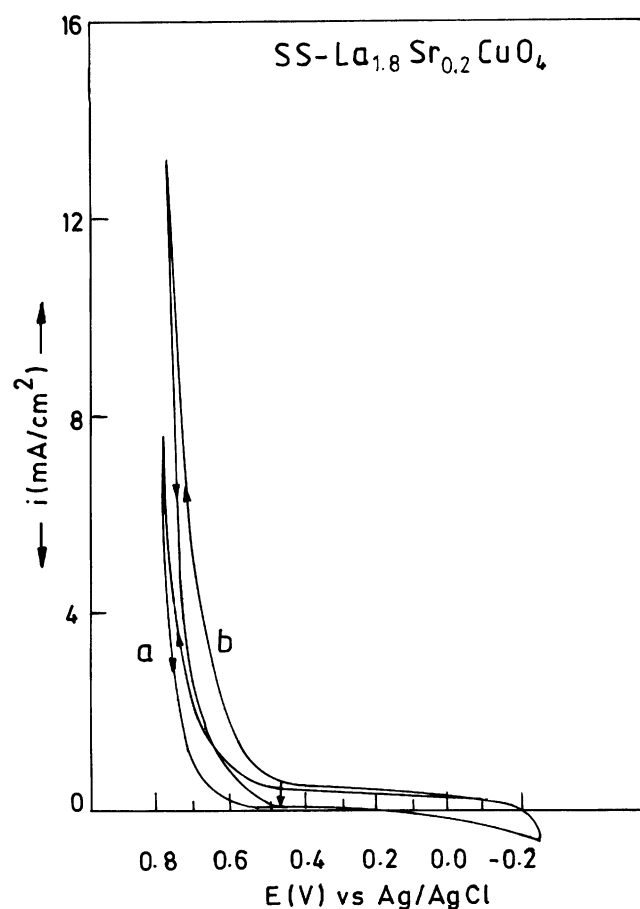


Fig. 7. Cyclic voltammogram of La_{1.8}Sr_{0.2}CuO₄ prepared by conventional ceramic method in (a) 1 M KOH and (b) 1 M KOH and 1 M CH₃OH mixture at the scan rate of 25 mV/s at RT.

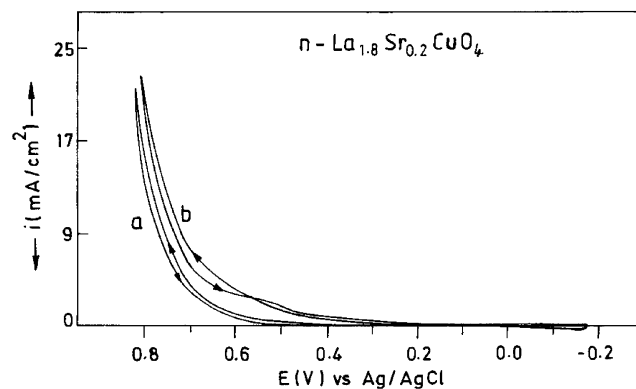


Fig. 8. Cyclic voltammogram obtained for methanol oxidation using nanocrystalline La_{1.8}Sr_{0.2}CuO₄ in 1 M KOH at the scan rate of 25 mV/s at RT.

Table 3

Comparison of nanocrystalline versus bulk cuprate for methanol oxidation in 1 M KOH at RT

Electrocatalyst	Methanol oxidation onset potential (V) versus Ag/AgCl	Activity at +0.6 V ^a <i>I</i> (mA/cm ²)
Nanocrystalline, La _{1.8} Sr _{0.2} CuO ₄	0.40	5.2 (2.7)
Bulk, La _{1.8} Sr _{0.2} CuO ₄	0.48	1.9 (1)

Numbers in bracket represents the activity factor for the comparison of nanomaterial with that of the bulk.

^a Activity was evaluated from the cyclic voltammogram.

charge region. This is because, as valence and conduction bands evolve from the initial diatomic states, upon the extension of the bonding in the lattice, unbound and partially bound surface (dangling or broken bonds) atoms or surface atoms with strained bonds introduce states within the band gap. Since the number of broken bonds or dangling bonds is higher for the oxide with smaller crystallite size, therefore the density of surface states is increased in the band gap [24].

The substituted lanthanum cuprates oxidize methanol at higher potentials compared to platinum in alkaline medium. The equilibrium between the electrode and the depolarizer depends on the position of the Fermi level of the electrode. By suitable substitutions at the A and B sites, and by controlling the particle size, the density of states as well as the existing field gradient can be altered so that these systems can be made to promote the oxidation process preferentially at lower potentials. This probably provides a selection criterion for designing at alternative materials for fuel cell applications.

4. Conclusions

The La_{1.8}Sr_{0.2}CuO₄ particles obtained by the polymer modified sol–gel method are spherical in nature and have a size in the nanoscale range (1–14 nm), as was evident from the transmission electron micrographs. On substituted oxide in nanocrystalline form, the onset potential is shifted cathodically and activity for methanol oxidation is nearly three times higher than that of the same material prepared by a conventional ceramic method. The increase in activity of the nanocrystalline material may be attributed to the

enhanced surface to volume ratio as well as increase in the density of surface states at the diffuse space charge layer in the solid.

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