Carbon monoxide is one of the most important reducing gases to be detected in combustion of hydrocarbon fuels, petroleum and automobile industries, heat-treating furnaces and, also in the first stages of fire. During the past four decades, gas sensors based either on the surface characteristics or the bulk properties of ceramics have been the subject of extensive research and development. New materials research endeavors are leading to the development of new solid-state devices for CO detection and metering. Nevertheless, even the most recent development in this area falls short of what is desired and required in real-life, e.g., selectivity, sensitivity, response-time and reversibility. This review attempts to take stock of the present day scenario of the advances made towards the development and performance of solid-state chemical sensors for carbon monoxide. In addition, some recent results on the development of CO sensors for NASA's proposed Manned Mars Mission are also presented.

INTRODUCTION

Harmful pollutants are generated by a host of industries such as chemical, pharmaceutical, ceramic, electronic and automobile. Among the gaseous pollutants, carbon monoxide is one of the most important reducing gases to be detected in the combustion of hydrocarbon fuels, heat treating and carburization furnaces, and also in the first stages of fire. The threshold weighted-average of CO level set by OSHA (Occupational Safety and Health Administration) and USEPA (United States Environmental Protection Agency) is 35 ppm per 8h duration for general public hygiene and safety. Given its toxic effect both in the event of short-term and long-term exposures, its continuous monitoring and quantification is of prime importance. Beside CO, there is a significant increase in air-borne NOx, SOx, CO2 and tropospheric (surface) O3. In fact, throughout the world there is an increasing concern about the minimization of the emission of noxious gases such as CO, NOx, SOx, and unburned hydrocarbons (CH4 and higher analogues) from automobile exhaust - the major mobile source of urban pollution (1). These emissions have a direct bearing on the corresponding increase in smog and acid rain. Smog is smoke-induced fog (SMoke-fOOG), resulting from condensation of water vapors in chimney gases and air on smoke and dust particles, acting as nuclei. It
should be pointed out that excessive smoke emission also reduces furnace efficiency, causing considerable heat loss (2).

During the past four decades, gas sensors based either on the surface characteristics or the bulk electrolytic properties of ceramics have been the subject of extensive research and development. The application of these sensors range from air-to-fuel ratio control in combustion processes such as in automotive engines and industrial furnaces to the detection of leakage of inflammable and toxic gases in domestic and industrial environments. The solid-state physical sensors, measuring pressure, temperature and other physical parameters have been commercially successful; less success has been achieved by their chemical counterparts, to measure low concentrations of gases in the ambient. Although the literature is abundant with a variety of sensor development efforts, it is important to note that most of these developments are based on rather empirical and/or trial and error methods. New materials research endeavors are leading to the development of new devices for gas detection and metering as well; nevertheless even the most recent developments in this area falls short of what is desired and required in real-life. Thus, there is a need to develop highly sensitive, fast-responding, miniaturized, portable, rugged and inexpensive sensor devices for potential health hazard gaseous species in air. The most popular class of these are the ones based on semiconducting oxides (such as ZnO, SnO$_2$, TiO$_2$, etc., and their doped varieties). These are produced in huge volume annually in the USA, Europe and Japan and used currently on a massive scale for the leak detection of inflammable gases such as CH$_4$, H$_2$, CO, cooking gas, etc. The most celebrated Taguchi Gas Sensors (TGS) or Figaro Sensors belong to this class. The semiconductor-based chemical sensors owe their popularity to small size, simple operation, high sensitivity and relatively simple associated electronics. However, most of them still suffer from non-selectivity. They also have poor shelf life and are relatively less stable at higher temperatures (3,4).

This paper attempts to take stock of the present day scenario of the advances made towards the development and performance of some of the solid-state sensors for CO gas. Wherever the information is available in the open literature, the functioning mechanisms of these devices have also been highlighted. In addition, some recent results on the development of CO sensors for NASA's proposed Manned Mars Mission are also discussed.

DEVELOPMENT OF CO SENSORS

The early attempts of gas sensing were targeted mainly towards the combustible gases that are also reducing in nature. These gases specifically included first hydrocarbons and subsequently cooking gas and town gas. Thus, understandably, there are not many documented evidences of attempts to develop CO gas sensors *per se*. The initial ‘claims’ of CO sensors were in fact a spin-off of the methods used for any combustible gas. However, it was subsequently recognized that most of these devices suffered from a basic shortfall, viz., the non-selectivity towards a particular species in a mixture of several gases. This led to more concentrated efforts in recent years towards development of
newer materials or intelligent modification of the existing ones to impart a certain degree of specificity in terms of amplified signal towards one particular gas in relation to others. With advances made in methods of material processing, material modification (surface or bulk), microstructural control, characterization techniques and most importantly the recognition to the crucial role played by catalysts, significant success has been achieved in developing highly selective and gas specific sensors in recent years. Thus, in some cases while traditional techniques are still in vogue, improvement in crucial sensing parameters such as, response time, signal reproducibility, surface/ bulk morphology retention, effect of thermal cycling, etc., has been made possible mainly by material tailoring. Equipped with these important materials processing and characterization tools, researchers have been engaged in developing highly gas-specific sensing devices including those for CO, with varying degree of success.

Attempts have been made to use the conventional YSZ-based devices in the mixed potential mode for CO, H₂ or hydrocarbons in combustion control systems albeit with unsatisfactory results. This was ascribed mainly to the inadequate EMF generated in the presence of reducing gases. Yamazoe and Miura (5) maintain that the main cause of this failure is associated with the use of Pt-electrodes. Being an active oxidation catalyst, Pt causes complete oxidation of the reducing gases at high temperatures, prior to their reaching the crucial 3-phase contact. On the other hand, temperatures lower than about 400 °C are inadequate owing to insufficient ionic conductivity of YSZ electrolyte. However, Okamoto et al. (6) have disclosed a gas sensor consisting essentially of an oxygen ion conducting electrolyte, one Pt-electrode and one alumina supported Pt-electrode, providing an interface for the 3-phases (solid electrolyte, alumina supported electrode and gas). Using this configuration, CO levels up to ~1000 ppm could be detected at temperatures above 250 °C. The upper limit of the operating temperature at which the sensor could be used to detect CO in the gas stream was about 450 °C, above which the sensor signal (in terms of EMF) became immeasurably small leading to erroneous results.

Maeda and Nagao (7) claimed to have used ZrMo₂O₈ as the electrode on the test gas side (containing CO) in a galvanic cell configuration with YSZ as the electrolyte. They correlated the EMF response of the cell to the ratio of CO/O₂, expressed in terms of the magnitude of incomplete combustion. The sensing mechanism of this sensor is not clearly understood or theoretically explained. Similar considerations have recently led to the use of an oxide-sensing electrode with stabilized zirconia electrolytes in the case of H₂S, H₂ and CO sensing (8-10). However, a further understanding and development of these or similar electrode materials might result in reliable combustion control sensors, where CO level in the gaseous mixture could be used as an index of the progress and/or completion of combustion process.

The most widely studied area of solid-state gas sensors is that based on semiconducting oxides. It has been long known that adsorption of foreign species on a semiconducting surface provides surface states that change the electrical properties as a result of adsorption and/or reaction (11-12). Significant progress has been made to utilize this change in the semiconductor property to quantify the presence of a specific reactive gas in a gaseous mixture. These oxides have been successfully employed as sensing
devices for the detection and metering of a host of gases such as CO, CO₂, H₂, H₂O, NH₃, SO₃, NOₓ etc., with varying degree of commercial success (13).

The report on a ZnO-based thin film gas sensor by Seiyama et al. (14) in 1962 gave rise to unprecedented development and commercialization of a host of semiconducting oxides, for the detection of a variety of gases over a wide range of composition. Simultaneous efforts were also made to improve the selectivity, sensitivity and response characteristics by modifying the surface chemistry by means of a catalyst (15). The working principle of the sensor devised by Seiyama et al. is based on the idea that, besides the reaction with oxygen, the surface and grain boundary resistance of the oxide is controlled by the adsorption of the gaseous species. Moreover, the chemical adsorption is very selective for different reactive gases. To increase the sensitivity of the sensor, 0.2 wt. % Pd was added to the sensor material. This sensor could detect ethanol and carbon monoxide. Following this, a number of investigations were reported to enhance the sensitivity and selectivity of sensors by means of additives (16).

In general, semiconductor materials are used as sensors of reducing agents, gases oxidizable by atmospheric oxygen, and gases such as H₂, CO, hydrocarbons and other organic gases and vapors. Most of these sensors are believed to operate by adsorption of oxygen on the surface, leading to a high resistance (for n-type semiconductors such as ZnO, SnO₂, TiO₂ etc.), and the resistance is lowered when a reducing agent reacts with this surface. The other important oxygen removal process of relevance is the dissociation of the lattice and formation of lattice defects. For this, imperfections (e.g., oxygen vacancies) must be mobile at the temperature of application. Being endothermic in nature, this occurs at low oxygen partial pressures and/or high temperatures.

In the case of an n-type semiconductor, such as SnO₂, the chemistry occurring on the surface involves two main reactions. In the first reaction, atmospheric oxygen chemisorbs on the surface, consuming electrons:

\[
O_2 + 2 e^- \rightarrow 2 O^{\text{ads}} \quad [1]
\]

This ionosorption of oxygen results in a decrease in conductivity whose effect is the largest at the constricted contacts between the grains of a sintered powder (grain boundaries). Equation [1] is in fact an oversimplified picture of the surface reaction, since it may also proceed via O₂⁻ or O²⁻. The doubly charged oxygen ion is in general excluded for adsorbed species, because such a high charge on the ion may lead to instability, unless the site has a high Madelung potential. In view of normally high reactivity of O⁻, relative to O²⁻, the latter is not expected to react significantly with the reducing gas and at moderate temperatures, may desorb or transform to O' (17,18).

The reducing gas present in the ambient produces a counter reaction:

\[
R + O^{\text{ads}} \rightarrow RO_{\text{des}} + e^- \quad [2]
\]
where the reducing gas removes the chemisorbed oxygen, frees up an electronic carrier and increases the conductivity of the semiconducting gas sensor. These two irreversible reactions, act in opposite directions and for a given concentration of the reducing gas, would reach a steady state.

Even though, in most of these sensors the primary mechanism of operation is through the changes introduced in surface conductivity, by chemical reactions occurring on the surface, the change in conductance depends in great deal on the physical nature of the sensor element. For example, for sintered pellets or powders, the changes in conductance are greatest at the grain boundaries. For thin films, the oxygen induced depletion width might involve the entire film, but thick films where this does not occur, may involve a combination of factors (19).

Among the various semiconducting oxide gas-sensing materials, those based on tin oxide are the most popular ones in their simple or modified form (20). However, one of the main problems with tin oxide as well as other gas sensors is their lack of selectivity. They appear to respond to a wide spectrum of reducing gases, thereby making it difficult to assign the signal to a particular gas of interest in a mixture of several reducing gases. One method to overcome this difficulty is the use of thermal cycling of the sensor element (21, 22). As different reducing gases react at different rates as a function of sensor temperature, varying the temperature in a cyclic manner could lead to unique signatures of the gas of interest. In some cases, thermal cycling has been reported to cause great increase in the sensitivity of detection. Besides this, two more techniques have been used for obtaining selectivity to some extent in semiconductor sensors for combustible gases. One is the use of "filters", where only the gas(es) of interest can reach the sensor, while the gases that are of no interest are adsorbed (23). The other, more common approach to selectivity is through the use of catalysts and promoters. In order to promote the gas sensitivity, additives of various kinds have been employed; these materials effectively influence the semiconducting properties of the sensor material. The reactions may proceed via the additives supported on the semiconductor sensor rather than directly on the sensor surface. Addition of a noble metal (such as Pt, Pd etc. (24)) or an alloy of noble metals (such as Pd/Au (25)) has been long known to enhance the sensitivity and selectivity of the sensor elements. While the noble metals Pd and Pt tend to catalyze complete combustion of hydrocarbons to CO₂ and H₂O, some oxides such as Cu₂O and V₂O₅ have been reported to cause partial and selective oxidation (23). In some cases, the oxides together with Pt or Pd have been used to impart some selectivity. For example, in the study of Nitta and Haradome (25, 26) and Chiou et al. (27), ThO₂ was added to increase the sensitivity to CO of a Pd- and MgO-catalyzed SnO₂ sensor. These authors reported that the addition of ThO₂ increased the CO sensitivity and decreased the hydrogen sensitivity. It was suggested that thoria removed the hydroxyl radicals from the SnO₂ surface, allowing more oxygen adsorption to accelerate the CO oxidation rate. However, such a reaction might be facilitated at fairly low temperatures only. In some cases use of elemental Cr and Sb has also been reported to bring about specificity. Nevertheless, the precise role of these additives is not known yet and the explanation for most of the observations is based on pure speculations (28, 29). Therefore, low selectivity, poor sensitivity at low gas concentrations and a lack of clear understanding of the sensing mechanisms are some of the problems associated with semiconductor sensors,
and are yet to be resolved. The sensitivity of laser-ablated thin films of SnO$_2$ containing Ag or Pd are shown to be a strong function of the nature of the catalyst employed and the temperature of operation (30). For example, the Ag-doped SnO$_2$ film were found active towards H$_2$ and CO (in that order) at ~ 175 °C, with no interference from CH$_4$. However, the sensitivity factor for H$_2$ and CO was ~ 80,000 and ~ 120, respectively, thereby enabling the gas recognition. On the other hand, the signature for CO and H$_2$ gas on Pd-doped SnO$_2$ films could not be differentiated up until around ~ 200 °C. In both cases, however, the sensitivity towards CO and H$_2$ became identical at temperatures ≥ 450 °C. Coles et al. (31) reiterate that the sintering temperature does play a crucial role in imparting selectivity to various reducing gases in the ambient. In addition, for a number of doped-SnO$_2$ compositions, they observed a power law relationship between the resistance and the gas concentration, of the type, $R = \text{[gas]}^β$, where [gas] represents the concentration of the gas (CO, H$_2$ or CH$_4$) in ppm.

Yamazoe (32) has stressed the need to differentiate the receptor function (to interact with the reactive gases) from the transducer function (to transduce the effect of interaction into signals). The receptor function is provided by the semiconductor surface and the foreign metals and/or oxides if present, while the transducer function largely depends on the microstructure of the sensing element, especially on the size of crystallites relative to the Debye length. Nevertheless, both these functions are strongly dependent on various factors (such as the grain size, role of metal sensitizer and gas-selective sensitization, etc.), which give rise to a rather complex outcome in sensitivity and selectivity. Based on XPS measurements on Pd-modified SnO$_2$ sensors, Yamazoe et al. (33) have distinguished two types of interactions, chemical and electronic, leading to sensitization. In chemical interaction, the additives assist the redox processes of semiconductive oxides, whereas in electronic interaction, the additives interact electronically with the semiconductor as a sort of electron acceptor or donor. This causes a change in the electronic states of the additive, which in turn causes a change in surface conductivity. Xu et al. (34) have studied the correlation between the gas sensing characteristics of SnO$_2$-based sensors, where SnO$_2$ grain size was controlled by the addition of several dopants. It was found that the gas sensitivity increased with decreasing crystallite size (of the order of 5-10 nm). They interpreted the observed correlation in terms of the relative magnitudes of the crystallite diameter (D) and the Debye length (L). As D decreases and becomes closer to 2L, the space charge region is believed to become more dominant in each crystallite of the sensing material. Thus the electric resistance would become more sensitive to the reactive gases. In the case of the sensor doped with rare earth- or alkaline earth metals or with Ni and Zn (more or less stable valency), the crystallite size was about 5 nm (close to 2L; for SnO$_2$ reported L = 3 nm). In these cases the gas sensitivity was found to be exceptionally high. Environmental monitoring with emphasis on CO levels in urban areas using screen-printed SnO$_2$-based thick film sensors has also been recently reported (35, 36).

CO SENSOR DEVELOPMENT FOR EXPLORATION OF MARS

NASA's Mars Surveyor Program 2003 Lander Mission and Mars 2005 Definition Studies Preparing for Human Exploration Mission require CO sensors for the following reasons. Mars atmosphere consists predominantly of CO$_2$ (~97%) with N$_2$ and Ar making
up the rest. This large amount of carbon dioxide is proposed as the primary source of in-situ propellant production (ISPP) and in-situ consumable production (ISCP). The CO$_2$ will be reduced to CO according to the following reaction:

$$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \tag{3}$$

The CO will then be reacted with hydrogen to form methane, which will eventually be used as a propellant fuel for Mars Ascent Vehicle (MAV). The oxygen thus generated would be utilized as the liquid oxidant (LOX) for the propellant as well as for the crucial life-support for the astronauts.

Therefore, in view of its toxic effect, the continuous monitoring of low levels of CO gas in the O$_2$ gas streams is life-critical. On the other hand, measurement of high concentrations of CO on the fuel side is desired as well, as this parameter reflects the conversion efficiency and hence becomes mission-critical. Thus, the concentration of CO to be monitored and metered ranges from very low (ppm region) to very high (percent) level. The development of CO sensors for this specialized application, however, differs from the terrestrial ones in that there is no interference issue with respect to moisture as there is no water either in the Mars atmosphere or formed during the above-mentioned CO$_2$ processing.

For this purpose, unlike single ceramic oxides used with or without a second phase (catalyst or other wise), intimate two-phase mixtures of well-established semi-conducting ceramic oxides have been exploited. The rationale behind this philosophy is that while each of the individual oxide in the mixture is capable of giving a response in presence of the reducing gas, a well-mixed combination of the two on the other hand, might give rise to a modified space charge region (SCR) at the point of necking and “hetero” inter-granular contacts. It was also envisioned that by virtue of the anticipated modification in the electronic structure in the “regions of significance”, such combination in some cases could display enhanced sensitivity to CO gas compared to a single oxide individually. In certain cases, double oxides having semi-conducting properties were also synthesized and tested for their response toward CO gas. The selection of oxide combination was based on a careful review of the relevant phase diagrams, possible phase transformations, coexisting phases, vapor pressure (in the case of volatile components) and possible phase-field shifts in the temperature range of use of these combination. To this end, suitable mixtures of Ti (IV), Sn (IV), W (VI) and Rh (III) oxides were investigated and the results are briefly presented in this paper.

**EXPERIMENTAL**

High purity (99.9% and better) oxides, all from Alfa Aesar, Johnson Matthey Company, MA, were first mixed in an agate mortar, followed by dry ball milling for 1 h in polystyrene bottles using stabilized zirconia balls as the milling media. The milled powders were extracted and milled gently again in an agate mortar to break away the agglomerates and homogenize the powder. A portion of the ball milled powders was also compacted into 12 mm diameter and 2 mm thick pellets (pressure ~1-1.2 ton/in$^2$).
In the case of titania bearing compositions, care was taken to avoid the transformation of the as-received anatase phase into rutile upon heat-treatment and/or during gas sensing experiments. For this purpose, the pellets bearing titania were fired in air at 727 °C for 1 to 4 h. According to reliable phase diagram, Rh$_2$WO$_6$ decomposes above 1130 °C into WO$_3$ and metallic Rh:

$$\text{Rh}_2\text{WO}_6 \rightarrow \text{WO}_3 + 2 \text{Rh} + 1.5 \text{O}_2 \quad [4]$$

**RESULTS AND DISCUSSION**

The dependence of sensitivity on concentration of a 90 mole % TiO$_2$-10 mole % SnO$_2$ pellet fired for 1h at 727 °C (90TS71), is shown in Fig. 1 at two temperatures. The sensitivity is defined as the ratio of film resistance (R) in background gas (O$_2$ + N$_2$) to that in the presence of a given concentration of CO in the stream (R$_g$). As can be seen, the signal (in terms of the sensitivity vs. CO concentration) at 500 °C is slightly better than that at 400 °C.

![Fig. 1. Sensing behavior of 90TS composite pellets fired at 727 °C/1h.](image)

The effect of firing time on the response of 90TS pellets fired at 727 °C is shown in Fig. 2. The sensitivity towards CO gas does not differ much in the two cases and hence soaking for 1h appears to be adequate for this composition. The response of thick films of 50 mol.% TiO$_2$-WO$_3$ (50TW) and WR3 (Rh$_2$WO$_6$ heated at 1150 °C/2h) in a gas stream containing up to 1000 ppm CO is compared with that of 90TS72 pellet in Fig. 3 while the comparative sensitivity of WR3 film and 90TS72 pellet to higher concentration (up to 20,000 ppm CO) is shown in Fig. 4.
Fig. 2. Sensing behavior of 90TS71 and 90TS72 composite pellets fired at 727 °C for 1 and 2h, respectively.

Fig. 3. Response of 50TW and WR3 films and 90TS72 pellet at 500 °C; 90TS72 data taken at ≥ 2000 ppm CO (see Fig. 4).

Fig. 4. Response of two different materials at 500 °C up to 20,000 ppm CO.
It can be clearly seen that in the low CO concentration range (which is important for ISCP), the 50TW film is superior to both the WR3 film and the 90TS72 pellet. As shown in Table 2, the slope of the sensitivity vs. CO concentration curve of 50TW film is 5 and 2.5 times greater than that of WR3 and 90TS72, respectively. Figure 4 highlights two points. First, in the higher CO concentration regime, the response of the WR3 film is superior to that of the titania-tin oxide composite with respect to sensitivity, but has no apparent advantage over the composite in the low concentration region (see Fig. 3). Second, sensors in thick film configuration are more sensitive compared to a pellet. This could be correlated to the difference in morphology in the two cases, where a higher level of open porosity in the case of thick film is likely to facilitate better access and transport of the oncoming gas through a film as opposed to through the bulk solid. Moreover, in the higher CO regime, WR3 is more sensitive (~ 4.5 times) than the 90TS72 pellet.

Table 1. Sensitivity of various oxides tested in resistive mode at 500 °C

<table>
<thead>
<tr>
<th>Material</th>
<th>Slope (sensitivity vs. CO)/ppm</th>
<th>CO range</th>
</tr>
</thead>
<tbody>
<tr>
<td>50TW</td>
<td>5e-04</td>
<td>≤ 1000 ppm</td>
</tr>
<tr>
<td>90TS72</td>
<td>2e-04 2e-04</td>
<td>≤ 1000 ppm 2000 ppm ≤ CO ≤ 20000 ppm</td>
</tr>
<tr>
<td>WR3</td>
<td>1e-04 9e-04</td>
<td>≤ 1000 ppm 2000 ppm ≤ CO ≤ 20000 ppm</td>
</tr>
</tbody>
</table>

CONCLUSIONS

A variety of sensors responsive to CO gas have been developed. These ceramic sensors are easy to use and offer a viable alternative to several conventional techniques such as gas chromatography and infrared absorption, and can also be used for hazardous gas alarms and leakage detectors. High temperature sensors measuring the equilibrium as well as the true oxygen concentrations and detectors capable of measuring the CO to O₂ ratio, which is a measure of the degree of combustion, are also available. In particular, the metal oxide semiconductors (MOS) offer a number of significant advantages for which reason they continue to be investigated. Their manufacturing does not require very high temperatures. They are also easier to fabricate and miniaturize than those based on organic materials or the conventional gate-technology. Most importantly, they do not require reference electrodes. Although extensive advances have been made in the sensor technology using MOS, problems such as poor selectivity with respect to the interference of ambient gases, a lack of understanding of the sensing mechanisms and aging have to be overcome before reliable instrumentation can be designed. Further research in this area should lead to the development of reliable ‘stand-alone’ sensor systems which when used with the available electronics and software, are anticipated to greatly aid in the design of intelligent industrial processes with efficient emission control.

In the light of the results shown above for resistive type sensors, several materials show promise of being capable of sensing and metering CO in concentrations up to
20,000 ppm. In almost all cases, the linearity of sensitivity \( \frac{R}{R_g} \) with gas concentration could be used for accurate measurement of unknown level of CO.

Further, the linear dependence of sensitivity on gas concentration could be translated into a simple electronic circuitry. However, whether this linearity is maintained at higher (> 20,000 ppm) CO concentration, is yet to be investigated. At low temperatures (\( \leq 400 ^\circ C \)), the sensor response becomes slower and the signal becomes smaller. This could be attributed to higher resistance exhibited by the materials at lower temperatures (typical n-type semiconducting ceramic oxides) and smaller change in resistance upon exposure to a reducing gas.

Thus, we have a choice of materials for low (\( \leq 1000 \) ppm) as well as high (up to 20,000 ppm) CO levels. At the low end 50TW has the greatest sensitivity. At higher concentrations, WR3 appears better, although we have not yet tested 50TW in this range.

Newer materials, processing techniques and conventional materials in new formats are expected to be the crucial players in the development of highly selective, fast responding and miniaturized sensors for a number of gases in the next decade.

ACKNOWLEDGMENT

We wish to thank NASA (Contract # NAG-10-274) and the Florida Space Grant Consortium for their support of this work.

REFERENCES