

# Catalysis Using Metal Oxides with Mixed Ionic -Electronic Conductivity for Clean Energy Electrochemical Systems



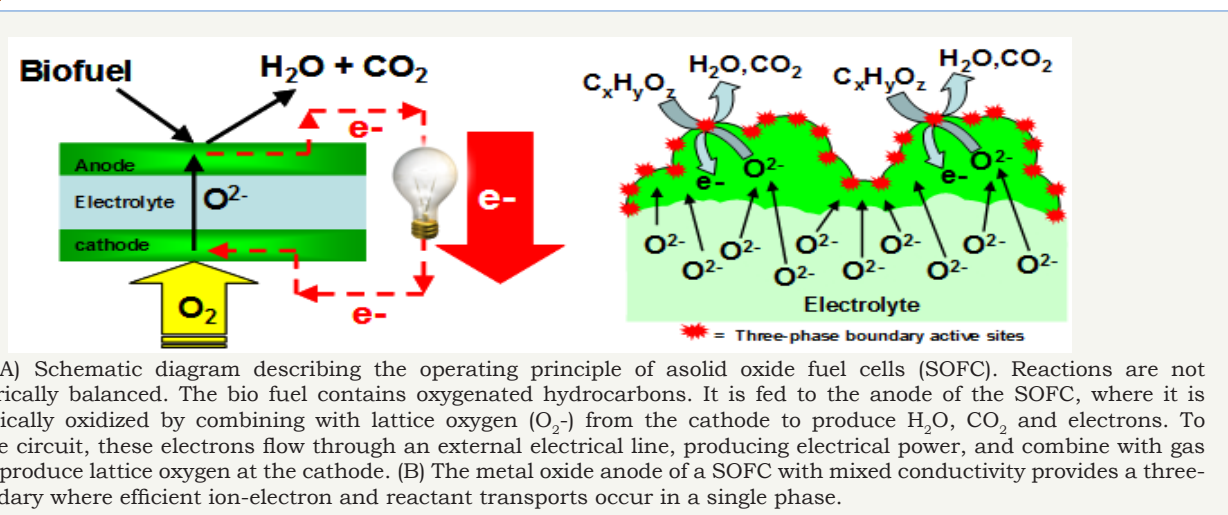
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## Introduction



**Figure 1:** (A) Schematic diagram describing the operating principle of asolid oxide fuel cells (SOFC). Reactions are not stoichiometrically balanced. The bio fuel contains oxygenated hydrocarbons. It is fed to the anode of the SOFC, where it is electrochemically oxidized by combining with lattice oxygen ( $O_2^-$ ) from the cathode to produce  $H_2O$ ,  $CO_2$  and electrons. To complete the circuit, these electrons flow through an external electrical line, producing electrical power, and combine with gas phase  $O_2$  to produce lattice oxygen at the cathode. (B) The metal oxide anode of a SOFC with mixed conductivity provides a three-phase boundary where efficient ion-electron and reactant transports occur in a single phase.

Direct bio-fuel solid oxide fuel cells (SOFCs) can play a key role in reducing greenhouse gases, reducing U.S. dependence on imported oil and moving us toward future energy independence [1-9]. Direct bio-fuel SOFCs can directly convert the chemical energy of bio-derived fuels into electrical energy as shown in Figure 1(A) [1,2]. In order to efficiently operate them, it is critical to develop a high-performance anode that can directly process bio-fuels [1-4]. Metal oxides with mixed conductivities, which transport both ions and electrons in a single phase, can be used as anodes for this application [5-14]. These oxides provide a three-phase boundary which is the area of contact among between the three phases necessary for electrochemical reactions to occur at the electrode: ion conducting phase, electron conducting phase, and gas phase (see Figure 1B). By balancing and controlling electronic and ionic bulk transport, the surface reaction rates and kinetics can be controlled [15-22]. Although the electrode materials have been used in various electrochemical applications [23-29], the fundamental relationship between ion-electron transport and catalytic activity with oxygenated hydrocarbons is still poorly understood. It is very important to address this scientific gap because high bio-fuel oxidation activity is an essential component

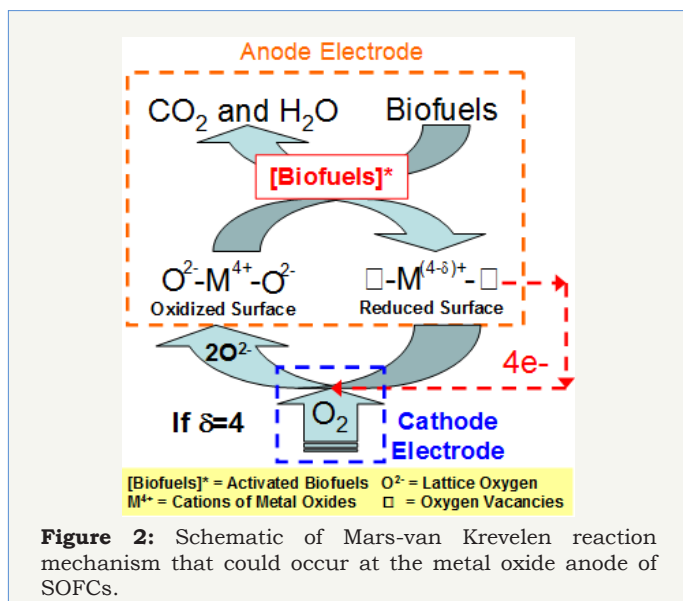
of a high-performance direct bio-fuel SOFC. The goal of this review is to summarize the working principle of direct bio-fuel SOFC, its performance limitations using the conventional catalytic materials, and its alternative catalytic materials for mitigating these limitations (especially metal oxides with  $MO_2$  structure (where  $M = Mo, W, Ru, Re, Os, Ir$ )).

## Literature Reviews

### Molecular structure of bio-fuels

One main distinction between petroleum fuels and bio-fuels is that petroleum fuels consisted of only carbon and hydrogen atoms while bio-fuels hold additional oxygen-containing functional groups [30-36]. Depending on the source of biomass and the chemical process used for chemical conversion, bio-fuels can have various functional groups and carbon-chain structures [37-42]. The different molecular structures of bio-fuels show different selectivity toward breaking C-H, O-H, C-O and C-C bonds, and different interaction with the metal oxide surface [43-47]. Thus, the bio-fuel oxidation activity and selectivity are strongly influenced by the molecular structure of bio-fuels.

## Operating principle of direct bio-fuel SOFC



A SOFC is an all-ceramic device that typically operates in the range 700-1000 °C [1-4]. Unlike low temperature polymer electrolyte membrane-(PEM) fuel cells, SOFCs hold particular promise for their ability to use CO as a fuel rather than being poisoned by it [48-51]. In addition, SOFCs do not require expensive noble metals to oxidize fuels. For a direct bio-fuel SOFC, the bio-fuels are fed to the anode, while molecular oxygen is fed to the cathode. In the high temperature range of interest to SOFC, it is believed that a Mars-van Krevelen mechanism is a dominant reaction pathway for oxidizing the fuels by reacting them with lattice oxygen from the electrolyte to produce electrons, CO<sub>2</sub>, and H<sub>2</sub>O (see Figure 2) [52-57]. According to this mechanism, the bio-fuels are first activated by breaking C-H or O-H bonds [58,59]. Typically, there is a strong charge interaction between these activated species and the cations of metal oxides [60,61]. As a result, the rate of the initial activation step strongly depends on the metallic property of metal oxides. Thus, controlling the metallic property of anode is very important to optimizing their fuel oxidation activity. The activated species are oxidized into CO<sub>2</sub> and H<sub>2</sub>O by insertion of lattice oxygen, which creates surface oxygen vacancies and reduces the surface. To continue this redox catalytic cycle, the reduced surface site is re-oxidized by releasing electrons via an external circuit to the cathode. In this sense, the lattice oxygen is the only oxygen source available for bio-fuel oxidation in SOFC. Consequently, the mobility and concentration of the lattice oxygen are closely related to the overall bio-fuel oxidation activity and selectivity [62-65]. The electrons generated at the anode combine with molecular oxygen to produce lattice oxygen at the cathode. This lattice oxygen diffuses toward the anode via the electrolyte to fill the vacancy, thereby completing the circuit. The flux of lattice oxygen from the cathode to the anode of SOFC is controlled by its operating cell voltage. The oxidation-degree and functional group of a bio-fuel can also significantly influence its activation step and affect its reaction selectivity [66-70]. Previous studies hypothesized that bio-fuels with a high

degree of oxidation would benefit their oxidation activity because they demand less lattice oxygen [71,72].

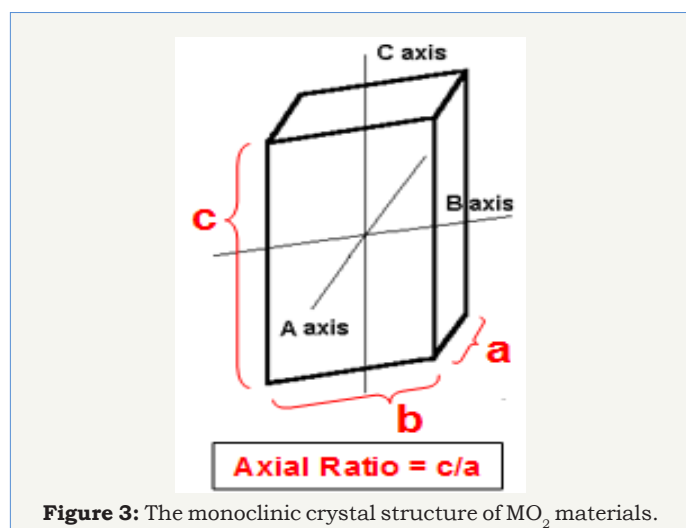
## Previously used catalytic materials in direct SOFCs

The most important materials problem to be addressed in the development of direct bio-fuel SOFCs is the anode. To operate efficiently for a long period of time, anode catalysts must have high bio-fuel oxidation activity and stability. Nickel-based electrodes have been widely utilized in direct fuel SOFCs [73-75]. Since it is a metal, Ni has a high electrical conductivity. To provide a thermal expansion match with the electrolyte and ionic conductivity to extend the three-phase boundary, Ni is conventionally mixed with yttria-stabilized zirconia (YSZ) to form a Ni-YSZ metal-ceramic composite (i.e., a cermet) [76]. However, the major disadvantage of the Ni-based electrode arises from its tendency to coke. Above 700°C, the active sites of Ni cermets are covered by a filamentous carbon coating [77-79]. To prevent coking, other researchers have replaced Ni with various metal oxides or mixed metal oxides, which possess high oxygen anion mobility. Due to the availability of lattice oxygen, the formation of coke is significantly retarded, while a high reforming activity for bio-fuels is retained [80-82]. However, the major disadvantage with these approaches to date is that the electronic conductivity of the materials is very low (e.g., CeO<sub>2</sub> has conductivity ~10 S/m at 25 °C). Because of the low electronic conductivity, these anodes show a high overpotential that leads to a low power density [76]. The University of Pennsylvania team improved the electronic conductivity of metal oxides by mixing them with catalytically inert transition metals [83]. For example, they replaced the Ni-YSZ anode with a Cu-CeO<sub>2</sub>-YSZ anode. The Cu provides excellent electronic conductivity but (unlike Ni) it is relatively catalytically inert. CeO<sub>2</sub> is used because of its high hydrocarbon oxidation activity, while YSZ provides the high ionic conductivity. This Cu-CeO<sub>2</sub>-YSZ anode shows good power density output and stability on various hydrocarbons and oxygenated hydrocarbons [4,83,84]. However, this anode has a disadvantage of increased complexity due to the increased number of required components and the requirement that reactions can only happen at the three-phase boundary.

## Alternative MO<sub>2</sub> catalytic materials in direct SOFCs

To decrease the complexity of electrode design, it is desired to use a single-phase catalyst that meets all of the anode requirements of direct SOFCs. The commonly suggested materials are the perovskite-structured oxides with a general chemical formula of ABO<sub>3</sub> [48,85-87]. However, our research team recently found that metal oxides with mixed conductivity such as MoO<sub>2</sub> also possess a very high catalytic oxidation activity toward biodiesel. MO<sub>2</sub> (where M=Mo, W, Ru, Re, Os, Ir) exhibits an unusual metallic-like electronic conductivity, which is not a common characteristic of most metal oxides [88,89]. Its electronic conductivity is attributed to a relatively high density of states in the valence band [90]. Figure 3 shows the distorted rutile crystal structure of MO<sub>2</sub> [91]. As the axial ratio of MO<sub>2</sub> decreases, its metal-metal bond distance becomes shorter thereby increasing the number of free valence

electrons available per bond [92]. Thus, the electronic conductivity of  $\text{MO}_2$  can be tuned by controlling its axial ratio. The easiest way for controlling  $\text{MO}_2$ 's axial ratio is by doping it with other  $\text{MO}_2$  that possesses higher or low axial ratios [93-97]. The axial ratio of  $\text{RuO}_2$  is 0.69 [98] while that of  $\text{MoO}_2$  and  $\text{WO}_2$  is between 1.00 and 1.02 [99,100]. As a small amount of  $\text{RuO}_2$  is doped into either the  $\text{MoO}_2$  or  $\text{WO}_2$  crystal structure, the unit cell volume should decrease and thus their electronic conductivity should increase. Similar to many metal oxides,  $\text{MO}_2$  also has high oxygen anion conductivity [90,101]. Its oxygen anion conductivity can be manipulated by controlling its metal-oxygen bond strength. Like its electronic conductivity, its metal-oxygen bond strength can be modified by doping it with other  $\text{MO}_2$  that possesses different metal-oxygen bond strength [15,102-105]. For example, the metal-oxygen bond of  $\text{MoO}_2$  is primarily "ionic" while that of  $\text{SiO}_2$  is "covalent." Consequently, the lattice oxygen mobility of  $\text{MoO}_2$  decreases by doping it with a small amount of  $\text{SiO}_2$  [106].



**Figure 3:** The monoclinic crystal structure of  $\text{MO}_2$  materials.

The metallic property of  $\text{MO}_2$  actively breaks various chemical bonds in bio-fuels leading to their high oxidation activity, while their ability to selectively transfer lattice oxygen to the carbon fragments minimizes coke formation during fuel oxidation [90,107-111]. Because of its unique mixed ion-electron conductivity, the three-phase boundary (the active electrode area) can be also extended over the entire electrode surface and thus overpotential losses at higher currents can be significantly reduced. Despite these exciting catalytic properties of  $\text{MO}_2$ , there has been a lack of studies to use it as the alternative working electrode material for direct bio-fuel SOFCs.

**Redox stability of  $\text{MO}_2$ :** Catalytic materials for efficient direct SOFCs must have both high and stable electrochemical activity under the various redox conditions [112-114]. Depending on the type of cat ion,  $\text{MO}_2$  will show different phase stability under a range of redox conditions [115-117]. We can increase the stability window of  $\text{MO}_2$  by doping it with redox stable metal oxides [15,103-105, 107]. For example, when  $\text{RuO}_2$  is doped with a small amount of  $\text{TiO}_2$ , its redox stability has been significantly increased

[118-120]. It is believed that  $\text{TiO}_2$  with a strong metal-oxygen bond decreases the oxygen mobility in  $\text{RuO}_2$  lattice as they substitute for Ru. A similar tactic has been used to develop a stable  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_3$  (LSCM) perovskite anode catalyst for SOFC, where unstable manganese oxide with a high fuel oxidation activity is atomically mixed with stable chromium oxide [121].

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