Improved the methanol electrooxidation and carbon monoxide tolerance for direct methanol fuel cells using strontium molybdate

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Abstract

Electrocatalysts possess high methanol electrooxidation (MOR) and carbon monoxide (CO) tolerance abilities to meet application requirements for enhanced performance of direct methanol fuel cells (DMFCs). Higher MOR and CO tolerance activities measured via cyclic voltammetry (CV) are achieved based on a strontium molybdate (SrMoO$_4$) mixed with Vulcan XC-72 carbon and loaded with 20% Pt. The synergistic effect of the bifunctional mechanism inducing the strontium molybdate is beneficial for removing CO-like intermediate products on the Pt surface, which leads to more Pt active sites released during MOR. The simultaneous unique structural formation of H$_x$MoO$_3$/H$_y$MoO$_3$ and SrMoO$_3$ in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ provides key synergistic effects for the 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C electrocatalysts, improving DMFCs performance. Results show that the 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C electrocatalysts exhibit excellent electrocatalytic activity for MOR (with a forward peak current density of 12.56 mA/cm$^2$ and large electrochemically active surface area (ECSA$_{H+}$) of 116.53 m$^2$/g, the best CO tolerance for electrooxidation of carbon monoxide (largest ECSA$_{CO}$ of 116.53 m$^2$/g), and the highest electric conductivity ($R_{ct}$ of 940 Ω•cm$^2$). Furthermore, the fabricated DMFC shows excellent long-term electrochemical stability after 1000 cycles and a maximum power density (1.42 mW/cm$^2$) higher than that with commercial 20%-Pt/C (1.27 mW/cm$^2$).

1. Introduction

Global warming has already created extreme weather globally. In recent years, the European Union energy and climate policy has required energy system transformations to reduce greenhouse gas emissions in 2050 to less than 80% of 1990 levels [1]. The conversion of carbon dioxide produced by feedstock into green methanol [2] is a key strategic factor for renewable energy and creation of a low-carbon economy. The manufacturing cost of renewable methanol will be gradually reduced by 2030, making it cheaper than coal and natural gas [2]. Methanol (CH$_3$OH) is a liquid fuel at room temperature, which makes it less toxic and provides higher octane value [3] than gasoline. It is also much easier to handle and store than pure H$_2$, another alternative fuel. Methanol is a key fuel for direct methanol fuel cells (DMFCs). Although DMFCs face difficulty when used in transportation power technology compared to well-known hydrogen fuels of polymer electrolyte membrane fuel cells, there is still opportunity for their use in portable power systems. Simultaneously, DMFCs are environmentally friendly when converting chemical energy from liquid methanol fuel to electrical energy as they only generate water and carbon dioxide (CO$_2$) byproducts. Until now, DMFCs have faced many problems such as the crossover of methanol fuel from the anode to cathode electrode [4]. The anode side of the DMFCs undergoes electrooxidation to CO$_2$, and the instability of the electrocatalysts occurs due to Pt poisoned by the absorbed carbon monoxide (CO) during methanol electrooxidation reaction (MOR) [5–6], as shown in Eqs. (1)–(3). CO adsorbed strongly on the surface of the Pt causes blockage of the Pt surface, reducing durability [7–8].

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]  (1)
2Pt + H₂ → 2Pt−H_ads (2)

CO₂ + 2Pt−H_ads → Pt−CO_ads + H₂O + Pt (3)

One method used to maintain the performance of DMFCs includes the addition of a high loading amount of Pt or Pt alloys on carbon as an electrocatalyst to increase CO tolerance [9]. Another method to improve Pt poisoned by CO is to introduce Pt loading on a metal oxide (MO) with carbon as electrocatalyst, which creates a synergistic effect from the bifunctional mechanism of Pt and MO. This synergistic effect enhances CO tolerance, as expressed in Eqs. (4)–(5) [10].

MO + H₂O → MO-OH_ads + H⁺ + e⁻ (4)

Pt−CO_ads + MO-OH_ads → Pt + MO + CO₂ + H⁺ + e⁻ (5)

Therefore, many studies have been performed with MOs incorporating Pt to create electrocatalysts that not only enhance MOR activity but also are not susceptible to carbon monoxide poisoning, for example, Pt/CeO₂-C [11], Pt-Co₃O₄ [12], Pt/NiO-C [13], Pt/SnOₓ-C [14], Pt−Ru/Al₂O₃-C [15], Pt/WO₃ [16], Pt/TiₓSn₁₋ₓO₂-C [17], and Pt/Ni-doped CeO₂-C [18]. To overcome CO poisoning is the loading of Pt on MoO₃. Through interaction with molybdenum bronzes (HₓMoO₃), clean Pt poisoned sites [19] are created during MOR. Justin et al. [20] reported a 128% higher peak current for MOR obtained by Pt-MoO₃/C compared to Pt−Ru/C. Therefore, MoO₃ [21] and Mo oxide-based catalysts, such as NiMoO₄ nanorods [22], Mo-doped CeO₂ (Ce₁₋ₓMoₓO₂₋₆) [23–24], Ti₁₋ₓMoₓO₂ [25], and (MoO₃)ₓSnO₂ [26], have been investigated.

In the present study, 20% Pt loading on strontium molybdate mixed with carbon black was prepared as the electrocatalyst to successfully improve MOR and CO tolerance in fabricated DMFCs. Strontium molybdate is a scheelite-type complex oxide [27] that consists of Sr²⁺ cations and (MoO₄)²⁻ anions. It has been used recently in electrocatalysts to increase hydrogen evolution reaction activity in acid water electrolytes [28] when applied to the electrochemical determination and photocatalytic degradation of diphenylamine [29] and tetracycline [30]. Thrane et al. [31] reported that SrMoO₄ catalysts can be used for the selective oxidation of methanol to formaldehyde. These recent studies have inspired our current investigation.

In this work, the influence of different calcination temperatures and different amounts of Sr mixed with the Mo contact during SrMoO₄ preparation on MOR and CO tolerance was investigated. Although commercial PtRu-C (E-TEK) catalyst has a higher MOR and more tolerance CO poisoning than commercial Pt/C [32–33], its cost is twice that Pt/C cause more limiting applied in DMFCs. Therefore, the results in this study focus on comparing with commercial Pt/C. The novel developed 20%-Pt/uncalcined Sr₀.₅Mo₀.₅O₄₋₅₋C electrocatalyst exhibits significantly enhanced catalytic activity for MOR and CO tolerance, as well as enhanced DMFCs performance compared with commercial 20%-Pt/C.
2. Experimental

2.1 Preparation of SrMoO₄

SrMoO₄ was synthesized by the polyol thermal method using 100 ml of strontium nitrate (Sr(NO₃)₂; Alfa Aesar) and 100 ml of ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O; ACROS) in molar ratios of 1:1, 0.5:1, 0.3:1, and 1:1.5 mixed with 40 ml of ethylene glycol (C₂H₆O₂; J.T. Baker®, USA) under magnetic stirring. Mixtures were heated at 120°C for 1 h and cooled to room temperature, producing a precipitate. The precipitate was centrifuged five times at 5000 rpm for 15 min each time. After centrifugation, the precipitate was washed with distilled water and heated overnight in an oven at 60°C. Finally, the precipitate underwent calcination temperatures of 200°C and 400°C for 1 h.

2.2 Pt/SrMoO₄-C preparation

A 1:1 weight ratio of 0.04 g SrMoO₄ was mixed with 0.04 g Vulcan XC-72 carbon black (with a Brunauer–Emmett–Teller surface area of 250 m²/g; Cabot Co.) with 40 ml of C₂H₆O₂ dispersed in a 100-ml beaker. The solution was then ultrasonicated for 15 min and underwent magnetic stirring for 1 h to form a uniform suspension. Next, 10 ml of 5.2 mg/ml (20%) hexahydrate (H₂PtCl₆·6H₂O; Alfa Aesar) in C₂H₆O₂ solution was supplemented to the suspension and stirred for 1 h. The pH of the suspension was adjusted to 11 by the drop-wise addition of 0.5 M sodium hydroxide (NaOH; Showa Chemical Industry Co., Ltd., Japan). The suspension was then heated to 140°C under reflux for 3 h. After the mixture was cooled, the precipitate was centrifuged at 5000 rpm three times for 15 min each. The precipitate was washed with distilled water, placed in a dish, and dried in an oven at 80°C for 24 h.

2.3 Material characterization

Raman spectroscopy measurements were performed at room temperature using a Raman spectrometer coupled to a microscope (Unidron, Taiwan) with a diode-pumped solid-state laser with a wavelength of 532 nm at 100 mW in the spectral range between 100 and 1100 cm⁻¹. The objective lens of the microscope resulted in a 1.2-mm diameter laser spot. SrMoO₄ structural properties were identified using X-ray diffraction (XRD) in a Rigaku (Japan) ultima IV rotating anode diffractometer with a Ni-filtered Cu-Kα radiation source (wavelength of 1.54 Å). The binding energies of different electrocatalyst elements were identified using X-ray photoelectron spectroscopy (XPS) with a VG Scientific ESCALAB 250 (UK) equipped with a dual Al X-ray source operated at 200 W and 15 kV. The beam size of the XPS X-ray source was 650 µm, and a hemispherical analyzer was operated in constant analyzer energy mode during measurements. The base pressure in the XPS analyzing chamber was maintained at 10⁻¹⁰ mbar. A nonlinear least-squares curve-fitting program with a Gaussian–Lorentzian production function, the Casa XPS program (Casa Software Ltd., UK), used to process XPS data. An adventitious C1s binding energy of 284.9 eV was set as the reference binding energy for charge correction. The morphology of the electrocatalysts was analyzed using scanning electron microscopy (SEM; JEOL JSM-6700F instrument) with energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) was
performed with a Philips FEI Tecnai G2F30 electron microscope with an acceleration voltage of 300 kV with a 1–25-nm probe size of EDS detector.

2.4 Electrochemical measurements

Electrochemical measurements were performed on a computer-controlled CHI 608E electrochemical analysis instrument (CH Instruments, Inc., USA). The electrocatalyst cyclic voltammetry (CV) curves of MOR were measured using a three-electrode cell system at room temperature within a potential range of −0.2–0.9 V at 50 mV/s in 100 ml of 0.5 M sulfuric acid (H$_2$SO$_4$; Honeywell) containing 1 M of methanol (CH$_3$OH; Honeywell).

An ink catalyst was prepared with 20 mg of catalyst dispersed in 1950 µl of ethanol (C$_2$H$_5$OH; Taiwan Sugar Corporation) and mixed with 50 µl of 20 wt.% Nafion solution (DuPont Co., USA) via sonication for 30 min. A working electrode was prepared by spreading 1 µl of the ink catalyst onto a 3-mm diameter glassy carbon electrode and dried at room temperature. Before using the working electrode, it was cleaned with alumina (1 and 0.3 µm grit size) polish paper. A Pt sheet electrode and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

CV curves of hydrogen adsorption–desorption for the electrocatalysts were obtained in a potential range between −0.2 V and 0.9 V at 50 mV/s in 100 ml of 0.5 M H$_2$SO$_4$ after ultrapure N$_2$ gas was flowed for 30 min. The electrochemically active surface area (ECSA$_H$) was calculated using the following equation:

$$\text{ECSA}_H [\text{m}^2/\text{g}] = \frac{Q_H}{(0.21 [\text{mC/m}^2] \times m_{\text{Pt}})}$$

where $Q_H$ [mC/cm$^2$] is the average of the integrated hydrogen adsorption and desorption area [mA/cm$^2$·V] obtained by Origin 8.5 software. Furthermore, the term 0.21 [mC/cm$^2$] in the equation represents the charge required to oxidize a monolayer of H$_2$ on Pt [34], and $m_{\text{Pt}}$ corresponds to the 20% Pt loading of the electrocatalyst on a disk electrode. $m_{\text{Pt}}$ was found to be 0.19 g/m$^2$ from the 13.61% Pt (theoretical 20% Pt) detected using a high-resolution inductively coupled plasma-mass spectrometer ELEMENT XR analyzer (Thermo Scientific, Waltham, MA, USA).

The CV curves of CO stripping for various electrocatalysts were obtained by purging CO gas (flow of 4 cc/min) into the 0.5 M H$_2$SO$_4$ solution under −0.12 V (versus Ag/AgCl) for 10 min and measured in the potential range of −0.2 to 0.9 V (versus Ag/AgCl) with a scan rate of 50 mV/s$^{-1}$ at 25°C. The ECSA$_{CO}$ was calculated using the following equation: $\text{ECSA}_{CO} [\text{m}^2/\text{g}] = \frac{Q_{CO}}{(0.42 [\text{mC/m}^2] \times m_{\text{Pt}})}$ [35]. $Q_{CO}$ [mC/cm$^2$] in this equation is the charge under the CO oxidation peak, which is related to the following oxidation process converting CO to CO$_2$: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$. The value of 0.420 [mC/m$^2$] corresponds to the charge required to oxidize a monolayer of CO adsorbed on Pt.

Electrochemical impedance spectra (EIS) were obtained at 0.4 V and from 100 kHz to 0.01 Hz in a 0.5 M H$_2$SO$_4$ containing 1 M CH$_3$OH mixture de-aerated with ultrapure N$_2$ gas (4 cc/min) for 30 min. The charge reaction resistances ($R_{ct}$) associated with the MOR [36] of the electrocatalysts were assessed by the diameter of the primary semicircle using Nyquist plots of EIS measurements.
2.5 Membrane electrode assembly fabrication and single-cell performance testing

The anodic catalyst ink was prepared with 12 mg of varying Pt/uncalcined $\text{Sr}_{0.5}\text{Mo}_{0.5}\text{O}_{4-\delta}-\text{C}$ catalyst content (i.e., 20%, 18%, and 15%) dispersed in 400 µl of ethanol, 100 µl of ethylene glycol, and mixed with 15 µl of 20 wt.% Nafion solution with 30 min sonication. The ink was then dropped on a 2.5 cm × 2.5 cm carbon paper (25BC, Hephass energy) and dried at 40°C for 24 h to create the anode electrode. The cathode electrode was prepared using commercial 20%-Pt/C at the same volume ratio as the 20%-Pt/uncalcined $\text{Sr}_{0.5}\text{Mo}_{0.5}\text{O}_{4-\delta}-\text{C}$ catalyst on a 2.5 cm × 2.5 cm carbon paper. A 3 cm × 3 cm Nafion® 117 membrane was used as the solid electrolyte. Before applying to the electrodes, the membrane was pretreated by immersion in 5% $\text{H}_2\text{O}_2$ solution at 80°C for 30 min and then rinsed with deionized (DI) water. Next, the membrane was immersed in 0.5 M sulfuric acid at 80°C for 30 min and finally rinsed with DI water. The treated membrane was stored in a beaker filled with DI water until used.

The membrane electrode assembly (MEA) had a 6.25 cm$^2$ active area, as shown in Fig. S1(a) and was hot-pressed on both sides between the anode/Nafion® film/cathode at 140°C with a pressure of 50 kg/cm$^2$ for 3 min. A simple single DMFCs was assembled without a bipolar plate, as shown in Fig. S1(b), to avoid electrocatalysts characteristic interface resistance effects. The DMFCs consisted of an air filled cathode tank, the MEA, and a 35-ml 20% methanol filled anode tank. The DMFCs performance was measured at ambient pressure and room temperature using the potentiostat/galvanostat of a CHI 608E electrochemical analysis instrument. The cell polarization curve was obtained for the electrocatalysts. The long-term durability of the catalysts was tested by conducting 1000 continuous potential cycles between 0.05 and 1.20 V at 50 mV s$^{-1}$.

3. Results And Discussion

3.1 Characterization of Pt/different calcination temperature $\text{Sr}_{0.5}\text{Mo}_{0.5}\text{O}_{4-\delta}-\text{C}$ catalysts

SrMoO$_4$ formation of uncalcined to a calcination temperature at 400°C was confirmed by XRD data in Fig. 1(a), which shows that the 2θ peak values are in good agreement with the characteristic peaks for the planes of tetragonal SrMoO$_4$ (JCPDS no. 08-0482). The Raman vibrational modes of SrMoO$_4$ compounds obtained at different Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ calcination temperatures correspond with those reported by Vidya et al. [37] and Szczancoski et al. [38] as shown in Fig. 1(b). Three Raman active mode peaks of MoO$_3$ are obtained at 219 cm$^{-1}$ ($A_g$, rotational rigid MoO$_4$ chain mode), at 288 cm$^{-1}$ ($B_{2g}$, δO = M = O wagging) in Fig. 2(c), and at 486 cm$^{-1}$ ($A_g$, $\nu_{as}$ O–M–O stretch and bend) [39] for uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$. However, these active mode peaks of MoO$_3$ do not appear at Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ calcination temperatures of 200°C and 400°C. Higher calcination temperatures more easily produce diffuse
phenomenon, which leads to increased crystalline structure formation of SrMoO$_4$. This results in no MoO$_3$ formation and no peak appearing.

The XPS analysis of Pt/different calcination temperature Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$C catalysts in the Sr 3d, Mo 3d, and Pt 4f regions are presented in Fig. 2. Figure 2(a) shows that the Sr 3d$_{5/2}$ and Sr 3d$_{3/2}$ doublets appear, as a result of spin-orbital splitting of Sr 3d peaks, at binding energies of 132.8 and 134.8 eV, which correspond to SrO structure [40]. This means that Sr$^{2+}$ is incorporated into the MoO$_4$$^{-2}$ structure at different Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ calcination temperatures. However, Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ under a calcination temperature of 400°C generates extra Sr 3d spectra divided into two peaks, at binding energies of 134.2 and 135.8 eV, corresponding to strontium carbonate (SrCO$_3$) [40], which depends on SrO capturing CO$_2$ in air [41].

The Mo 3d doublet consisted of two distinct chemical states on Mo$^{6+}$ and Mo$^{5+}$ for different calcination temperatures of Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$, as shown in Fig. 2(b). The peaks of Mo$^{5+}$ 3d$_{5/2}$ and 3d$_{3/2}$ were located at 232.7 and 235.6 eV, respectively. The Mo doublets located at 233.8 and 237.2 eV proved that the Mo$^{6+}$ chemical state existed [42] in the Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$. The relative areas of integrated peak intensities of Mo$^{5+}$ decreased and, in contrast to that of Mo$^{6+}$ increased with calcination temperature increase, as shown in Table 1. The Mo$^{6+}$ relative area increased, meaning more SrMoO$_4$ compound formation with increasing calcination temperature.

In addition, the Pt 4f region displays spin-orbit splitting doublet peaks of 4f$_{7/2}$ and 4f$_{5/2}$ for Pt/various Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$/C, as shown in Fig. 2(c). All the Pt 4f signals consist of three doublets that can be attributed to different valence states of Pt. The first doublet peaks at approximately 71.2 and 74.5 eV are attributed to metallic Pt (Pt$^0$) [43]. The second doublet peaks at approximately 72.3 and 75.5 eV can be assigned to Pt$^{2+}$ species of PtO or Pt(OH)$_2$ due to surface oxide/hydroxide [44]. The third doublet peaks at approximately 74.1 and 77.2 eV correspond to Pt$^{4+}$ of PtO$_2$[45]. The relative area of integrated peak intensities for Pt/different calcined temperature Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$/C are shown in Table 1. Pt loading on Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ with calcination temperatures of 200 °C and 400 °C caused increased PtO and PtO$_2$ formation with less or no MoO$_3$ formation.
Table 1
Relative area of Mo 3d and Pt 4f from XPS of Pt/different calcination temperature Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C electrocatalysts.

| Electrocatalysts                  | Mo$^{5+}$ (%) | Mo$^{6+}$ (%) | Pt$^0$ (%) | Pt$^{2+}$ (%) | Pt$^{4+}$ (%) |
|----------------------------------|---------------|---------------|------------|--------------|--------------|
| Pt/Uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C | 82.6          | 17.4          | 54.0       | 34.4         | 11.6         |
| Pt/200 Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C     | 66.1          | 33.9          | 29.3       | 58.8         | 11.9         |
| Pt/400 Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C     | 60.5          | 39.5          | 27.1       | 48.6         | 24.3         |

The particle shape of uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ was donut-like or flower-like, as indicated by the SEM image in Fig. 3(a). These results are similar to the images reported by Wannapop et al., wherein donut-like SrMoO$_4$ was produced using the microwave-hydrothermal process [46]. Elemental mapping images indicate that the Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C catalysts contain Pt, Sr, Mo, O, and C elements, as shown in Fig. 3(b)–(f). These results indicate the successful incorporation of Pt loading into the uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C. Figure 4(a) shows TEM images of Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C with Pt particles, ranging in size from 2 to 2.5 nm, deposited. The HRTEM image (Fig. 4(b)) shows lattice fringes with $d$ spacings of 0.325 and 0.226 nm, which are attributed to SrMoO$_4$ (112) and Pt (111), respectively. EDS results confirmed the simultaneous existence of Pt, Sr, and Mo elements in the Pt/Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C, as shown in Fig. 5(c).

3.2 MOR and CO tolerance for strontium molybdate with different calcination temperatures

Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ was prepared using Sr and Mo precursors mixed with a molar ratio of 1:1 under different calcination temperatures (i.e., uncalcined, 200°C, and 400°C). The CV of 20%-Pt loaded electrocatalysts mixed with carbon is shown in Fig. 5(a). The hydrogen adsorption and desorption peaks obtained between −0.2 and 0.1 V are shown in Fig. 5(b). The average areas were used to calculate the ECSA$_H$. The removal of incompletely oxidized carbonaceous species formation is demonstrated by the forward current density peak of potentials [47] during MOR. All electrocatalysts have a similar forward current density peak of potentials, and the oxidation peak potentials in the reverse scan are similar in Fig. 5(a). The forward peak current density and ECSA$_H$ decreases for Pt/Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C with increasing Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ calcination temperature in the following order: uncalcined > 200°C > 400°C, as shown in Table 2. Among these electrocatalysts, the uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ possessed the highest MOR activity and a forward peak current density, and ECSA$_H$ larger than the commercial Pt/C. In addition, the striking MOR properties of Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$/C are noted in Fig. 5(b), which shows a peak between 0.08 and 0.32 V contributes to the formation of H$_x$MoO$_3$ by hydrogen adsorption on Pt and migration onto the MoO$_3$ surface [20] in Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ follows the mechanism described by Eq. (6) [48]. H$_x$MoO$_3$
can oxidize adsorption intermediates (CO or CH$_2$O$_{ads}$, 0 ≤ z ≤ 4) on Pt, as shown by Eq. (7) [49]. However, H$_x$MoO$_3$ provides charge transport across the support and can be easily oxidized on the Pt to form H$_x$MoO$_3$ with less hydrogen (H$_y$MoO$_3$) (0 < y < x < 2), which plays a role as proton acceptor [20]. This can also oxidize adsorption intermediates on Pt, as shown by Eq. (8) [50].

MoO$_3$ + xPt-H → H$_x$MoO$_3$ + xe$^-$ + xPt (6)

Pt→ CO$_{ads}$ / Pt→ CH$_2$O$_{ads}$ + H$_x$MoO$_3$ + H$_2$O → CO$_2$ + Pt + H$_{x+2}$MoO$_3$ (7)

Pt→ CO$_{ads}$ / Pt→ CH$_2$O$_{ads}$ + H$_y$MoO$_3$ + H$_2$O → CO$_2$ + Pt + H$_x$MoO$_3$ (8)

In Fig. 5(b), the peak demonstrates the existence of H$_x$MoO$_3$/ H$_y$MoO$_3$, which can quickly remove intermediates from Pt surfaces and significantly accelerate the transformation of adsorbed intermediates to CO$_2$ [50]. This facilitates methanol adsorption on Pt sites in the presence of MoO$_3$, thereby maintaining higher MOR activity. The results demonstrate that MoO$_3$ compound formation is important. The MoO$_3$ compound in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$ structure is confirmed by Raman data, as shown in Fig. 1(c).

In addition, the charge transfer resistance ($R_{ct}$) and Nyquist plots of the various electrocatalysts were fitted with the corresponding equivalent circuit, as shown in Fig. 5(c) and its inset. For the circuit, $R_s$ represents the solution resistance, $R_o$ is the contact resistance between the catalyst and the support electrode, and the constant phase element (CPE) is the double-layer capacitance, which is associated with the adsorption of intermediates formed during MOR [36]. The results show that the $R_{ct}$ increased with increasing Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$-C calcination temperature, indicating decreased electrical conductivity. The highest electrical conductivity obtained by the Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$-C was better than that by commercial Pt/C, indicating that the ion transfer rate was faster and leads to the best electrocatalytic activity for MOR.

CO stripping voltammetry for various electrocatalysts is as shown in Fig. 5(d). The peak area appeared in the difference in current density between the 1st cycle and that of the 2nd cycle, indicating the amount of CO stripped off from the Pt surface [51]. The ECSA$_{CO}$ decreased with increasing Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$ calcination temperature (Table 2). Since CO species are the main poisoning intermediate during MOR when employing Pt catalysts, the uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$ catalysts may assist the removal of the poisoning intermediate and thus offer excellent CO electrooxidization ability to the electrocatalyst system, recovering reaction sites for methanol oxidation [52]. The enhanced CO tolerance of the Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$-C could be attributed to the strengthened synergistic effect from both Pt and SrMoO$_4$ from the uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4−δ}$. Therefore, SrMoO$_4$ can facilitate the electrooxidation of adsorbed CO at lower potentials, which is described by the bifunctional mechanism in Eqs. (8)–(9) wherein the OH is adsorbed on the surface of the MO, which may oxidize the CO on the surface of Pt [52–53].

SrMoO$_4$ + H$_2$O → SrMoO$_4$−OH$_{ad}$ + H$^+$ + e$^−$ (8)
Pt(CO)$_{ad}$ + SrMoO$_4$–OH$_{ad}$ → Pt + SrMoO$_4$ + CO$_2$ + H$^+$ + e$^-$ (9)

The highest relative area of Mo$^{5+}$ contact was in the uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$, higher than that of 200°C and 400°C, which is attributed to MoO$_3$ formed from distorted octahedra [54] and indicates the generation of a higher concentration of oxygen vacancies [55]. The generation of oxygen vacancies allows better electron transfer from the catalysts to the Pt [56]. Moreover, the cations in the vicinity of the oxygen vacancies in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$ are reduced, which triggers electronic interactions between reduced cations and Pt atoms. This gives rise to interactions known as strong metal-support interactions [57], which help improve electrocatalytic MOR performance.

In addition, the binding energy peak of Pt$^0$ is the dominant component of the Pt 4f due to its important role in supplying available active Pt sites for methanol adsorption for MOR. Therefore, the results show that Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C generates the largest relative area of Pt$^0$ peak, which is 54.0% higher than that of 200°C (29.3%) and 400°C (27.1%).

Uncalcined MoO$_{3-δ}$ was prepared to compare with Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C. The MOR, EIS, and CO tolerance are shown in Figs. 5. Unfortunately, Pt/uncalcined MoO$_{3-δ}$-C obtained lower MOR and CO tolerance with larger $R_{ct}$ characteristics. XRD results of uncalcined MoO$_3$ were analyzed in our previous study [58] and indicated MoO$_x$ or molybdenum trioxide hydrate (MoO$_3$•H$_2$O) compounds. Therefore, when Sr was mixed with Mo precursors to prepare SrMoO$_4$, the substitutional incorporation of Sr$^{2+}$ ions at Mo$^{6+}$ sites depends on the ionic radius of Sr$^{2+}$ (1.26 Å), which is larger than that of Mo$^{6+}$ (0.41 Å) [27]. This leads to immediate formation of SrMoO$_4$ crystal structure without calcination. The result of Sr doping in MoO$_3$ compounds is enhanced by MOR and CO CO tolerances.

| Electrocatalysts                  | Forward peak current density (mA/cm$^2$) | ECSA$_H$ (m$^2$/g) | $R_{ct}$ (Ω cm$^2$) | ECSA$_{CO}$ (m$^2$/g) |
|----------------------------------|----------------------------------------|--------------------|---------------------|------------------------|
| Pt/uncalcined MoO$_{3x-C}$       | 9.50                                   | 45.37              | 1410                | 62.78                  |
| Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C | 12.56                                  | 116.53             | 940                 | 168.14                 |
| Pt/200 Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C | 4.41                                   | 25.12              | 4600                | 23.57                  |
| Pt/400 Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$-C | 3.62                                   | 22.52              | 5682                | 20.32                  |
3.3 MOR and CO tolerance of strontium molybdate oxide prepared with different Sr and Mo ratio contacts

The MOR was determined for Pt/uncalcined SrMoO$_4$-C prepared with different mole ratios of Sr and Mo precursors: 1:1, 2:1, 3:1, and 1:2, named Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$, Sr$_{0.67}$Mo$_{0.33}$O$_{4-δ}$, Sr$_{0.75}$Mo$_{0.25}$O$_{4-δ}$, and Sr$_{0.3}$Mo$_{0.67}$O$_{4-δ}$, respectively. The results are shown in Fig. 6(a). The forward peak potentials on the Pt- various SrMoO$_4$/C catalysts were observed at approximately 0.40–0.43 V in the forward scan. Furthermore, the CV of MOR, CO tolerance, and EIS of the various catalysts is shown in Fig. 6(b)–(d). Their forward peak intensities, ECSA$_{H}$, ECSA$_{CO}$, and $R_{ct}$ are shown in Table 3. The results showed that the forward peak intensities, ECSA$_{H}$, and ECSA$_{CO}$ decreased in the following order: Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$ > Sr$_{0.3}$Mo$_{0.67}$O$_{4-δ}$ > Sr$_{0.67}$Mo$_{0.33}$O$_{4-δ}$ > Sr$_{0.75}$Mo$_{0.25}$O$_{4-δ}$. The $R_{ct}$ from the EIS, in increasing order, are as follows: Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$ < Sr$_{0.3}$Mo$_{0.67}$O$_{4-δ}$ < Sr$_{0.67}$Mo$_{0.33}$O$_{4-δ}$ < Sr$_{0.75}$Mo$_{0.25}$O$_{4-δ}$. The results showed that the largest ECSA$_{H}$, and ECSA$_{CO}$ and the smallest $R_{ct}$ were obtained by Pt/Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$-C electrocatalysts. These values were lower than that of commercial Pt/C catalysts. The uncalcined SrMoO$_4$ prepared with a 1:1 mole ratio of Sr and Mo precursors obtained the best activity for MOR and CO tolerance. Unfortunately, the structure of the prepared SrMoO$_4$ with different Mo and Sr ratios was difficult to define using XRD (Fig. S2) due to these catalysts having the same 2θ peaks as SrMoO$_4$ structures. These electrocatalysts certainly affect Pt morphology when Pt is loaded on the electrocatalysts, as confirmed by XPS. The binding energy of Pt 4f XPS and relative area Pt$^0$ of Pt/ various SrMoO$_4$-C are shown in Fig. 7(a) and Table 4. The results showed that the relative area of Pt$^0$ decreased and oxidized Pt$^{2+}$ and Pt$^{4+}$ increased with increasing amount of Sr contact. The Pt-Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$-C electrocatalysts obtained the largest relative area of metallic Pt$^0$, higher than commercial Pt/C and with other mole ratios of Sr and Mo precursors, which confirms that Pt/Sr$_{0.50}$Mo$_{0.50}$O$_{4-δ}$-C has the best MOR and CO tolerances.

From the Mo 3d XPS, the binding energy of Mo$^{5+}$ was positively shifted when Sr contact mole ratio increased from 0.67 to 0.75, as shown in Fig. 7(b). This suggests that more Sr$^{2+}$ ions incorporated MoO$_4^{2-}$. Therefore, a lower amount of MoO$_3$ formation is demonstrated by decreasing intensities of the peak between 0.08 and 0.32 V, as shown in Fig. 6(b). In addition, when the Sr contact mole ratio was 0.75, binding energy peaks of Sr$^{2+}$ for SrCO$_3$ formed in Fig. 6(c). This could be the influence of less metallic Pt$^0$ formation, causing decreased MOR performance. Furthermore, the Mo$^{6+}$ binding energy peaks were negatively shifted when the Mo contact was increased to 0.67. This suggests that less SrMoO$_4$ production could reduce the synergistic effect of the bifunctional mechanism, resulting in lower MOR and CO tolerances.
Table 3
MOR, CO tolerances and $R_{ct}$ of various electrocatalysts.

| Electrocatables           | Forward peak current density (mA cm$^{-2}$) | ECSA$_H$ (m$^2$g$^{-1}$) | ECSA$_CO$ (m$^2$g$^{-1}$) | $R_{ct}$ (Ω cm$^2$) |
|---------------------------|---------------------------------------------|---------------------------|---------------------------|---------------------|
| Pt/C                      | 8.87                                        | 63.81                     | 52.61                     | 1220                |
| Pt/Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C | 12.56                                       | 116.53                    | 168.14                    | 940                 |
| Pt/Sr$_{0.67}$Mo$_{0.33}$O$_{4-\delta}$-C | 8.87                                        | 25.12                     | 44.38                     | 1590                |
| Pt/Sr$_{0.75}$Mo$_{0.25}$O$_{4-\delta}$-C | 6.35                                        | 24.15                     | 31.20                     | 1900                |
| Pt/Sr$_{0.33}$Mo$_{0.67}$O$_{4-\delta}$-C | 6.58                                        | 19.90                     | 37.95                     | 1860                |

Table 4
Relative area of Pt 4f XPS for various electrocatalysts.

| Materials                      | Pt$^0$ (%) | Pt$^{2+}$ (%) | Pt$^{4+}$ (%) |
|--------------------------------|------------|---------------|---------------|
| Pt/C                           | 52.6       | 36.4          | 11.0          |
| Pt/Sr$_{0.50}$Mo$_{0.50}$O$_{4-\delta}$-C | 54.0       | 34.4          | 11.6          |
| Pt/Sr$_{0.67}$Mo$_{0.33}$O$_{4-\delta}$-C | 42.8       | 42.3          | 14.9          |
| Pt/Sr$_{0.75}$Mo$_{0.25}$O$_{4-\delta}$-C | 39.2       | 43.8          | 17.0          |
| Pt/Sr$_{0.33}$Mo$_{0.67}$O$_{4-\delta}$-C | 38.3       | 47.0          | 14.7          |

3.4 DMFCs performance and cycling performance tests

Figure 8(a) shows the CV curve for DMFCs performance of commercial 20%-Pt/C and uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_4$-C with different amounts of Pt. The results showed a maximum power density of 1.42 mW/cm$^2$ for 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_4$-C, which is higher than that of commercial 20%-Pt/C (1.27 mW/cm$^2$). Furthermore, the power density of 18%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_4$-C (1.29 mW/cm$^2$) is similar to that of commercial 20%-Pt/C, which demonstrates that using 2% less Pt loading can maintain the same DMFCs performance as commercial 20%-Pt/C. Unfortunately, 15%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_4$-C has a lower power density (0.84 mW/cm$^2$).
The cycling performance test of the commercial 20%-Pt/C and 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C electrocatalysts in MOR on performing 1000 continuous cycles in a 0.5 M H$_2$SO$_4$ containing 1 M CH$_3$OH mixture is shown in Fig. 8(b). Clearly, the current density of both electrocatalysts decayed when the number of cycles increased. As the number of cycles increases, intermediate carbonaceous species such as CO begin to accumulate on the electrode surface and may poison the Pt and decrease the oxidation current [58]. The 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C catalyst was able to maintain a higher maximum current density than that of the commercial 20%-Pt/C catalyst for the entire time at all cycles. In addition, uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ simultaneously contains SrMoO$_4$ and MoO$_3$ compounds, which play a role in CO tolerance. The mechanism of CO tolerance for Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C involves two simultaneous reactions, as shown in Fig. 9. The first reaction results in H$_x$MoO$_3$/H$_y$MoO$_3$ formation in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ under MOR, which helps to remove intermediates from Pt surfaces and accelerates the transformation of adsorbed intermediates to carbon dioxide. The second reaction obtains Pt and SrMoO$_4$ compounds in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ and generates the synergistic effect of the bifunctional mechanism.

4. Conclusions

In the present study, strontium molybdate was successfully prepared, mixed with carbon, loaded with 20% Pt, and used as an electrocatalyst for MOR and CO tolerance in a DMFCs. Tetragonal SrMoO$_4$ structure is the main compound for strontium molybdate. Strontium molybdate prepared with increased calcination temperature and increased Sr and Mo precursor contact ratios (larger than 1 mole ratio) resulted in reduced MOR and CO tolerance. The best MOR and CO tolerances and electrical conductivity were obtained by 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C, which showed improved DMFCs performance and improved cycling performance after 1000 cycles. This optimum strontium molybdate and contact ratio is beneficial for removing CO-like intermediate products on the Pt surface, which leads to more Pt active sites released during MOR. The simultaneous unique structural formation of H$_x$MoO$_3$/H$_y$MoO$_3$ and SrMoO$_3$ in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ provides key synergistic effects for the 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C electrocatalysts, improving DMFCs performance. These structures can simultaneously perform two working reactions during CO tolerance. The first reaction includes H$_x$MoO$_3$/H$_y$MoO$_3$ formation in uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ under MOR to help remove intermediates from Pt surfaces, reduce poisoned Pt, and accelerate the transformation of adsorbed intermediates to carbon dioxide. The second reaction includes both Pt and SrMoO$_4$ compounds in 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C, which generate a synergistic effect of the bifunctional mechanism that provides active oxygen for removal of CO on the Pt surface. Therefore, 20%-Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C electrocatalysts have potential as anode materials with a DMFCs performance 1.1 times higher than commercial 20%-Pt/C.

Declarations

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Figures

![Figure 1](image1)
![Figure 2](image2)

**Figure 1**

(a) XRD of Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ under different calcination temperatures. (b) Raman of Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$ under different calcination temperatures, and (c) uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$.

**Figure 2**

(a) Sr 3d, (b) Mo 3d, and (c) Pt 4f XPS of Pt/different calcination of Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$C.
Figure 3

(a) SEM image and (b)–(f) EDS elemental mapping of Pt/uncalcined \( \text{Sr}_{0.5}\text{Mo}_{0.5}\text{O}_{4-\delta}\)-C electrocatalysts.

Figure 4

(a) TEM image, (b) lattice fringes, and (c) EDS of Pt/uncalcined \( \text{Sr}_{0.50}\text{Mo}_{0.50}\text{O}_{4-\delta}\)-C electrocatalysts.

Figure 5
(a) CV curves of MOR, (b) hydrogen electroadsorption voltammetry of Pt/C and Pt/different calcination Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$/C electrocatalysts. (c) EIS and (d) CO stripping voltammetry on Pt/C and Pt/different calcination temperature Sr$_{0.5}$Mo$_{0.5}$O$_{4-δ}$/C electrocatalysts.

Figure 6

(a) CV curves of MOR, (b) hydrogen electroadsorption voltammetry, (c) Nyquist plots, and (d) CO stripping voltammetry for various electrocatalysts.
Figure 7
(a) Pt 4f (b) Mo 3d, and (c) Sr 3d XPS for various electrocatalysts.

Figure 8
(a) DMFC performance and (b) the number of cycles of commercial 20%-Pt/C and uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$-C catalysts with different Pt loading contents.
Figure 9

CO stripping of mechanism of Pt/uncalcined Sr$_{0.5}$Mo$_{0.5}$O$_{4-\delta}$.

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