



Molten silver as a direct carbon fuel cell anode

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HIGHLIGHTS

- ▶ Direct carbon oxidation is possible in molten Ag anode of solid oxide fuel cells.
- ▶ The molten Ag anode impedance is very high.
- ▶ The impedance of the electrode is limited by diffusion of oxygen in the Ag phase.
- ▶ Potential is governed by dissolved oxygen concentration in Ag at the electrolyte.
- ▶ In Ag–Sb alloy anode with charcoal, potential of Sb–Sb₂O₃ equilibrium is observed.

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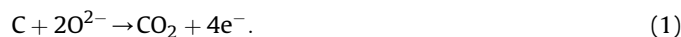
ABSTRACT

Molten Ag and Ag–Sb alloy have been examined as anodes in direct carbon solid oxide fuel cells (SOFC) at 1273 K. For Ag, an open-circuit voltage (OCV) typical of that expected for carbon oxidation, 1.12 V, was observed when charcoal was mixed with the molten Ag. However, the anode impedance was high, ~100 Ω cm². The nature of the electrode losses was investigated by measuring the voltage–current characteristics of a cell with Ag but no carbon at the electrode, while ramping the voltage under fuel cell and electrolysis conditions. The results indicate that the cell potential is governed by the oxygen concentration in the Ag at the electrolyte interface. Using this and a model of carbon oxidation within the molten Ag, it is determined that the impedance of the electrode is limited by diffusion of oxygen in the Ag phase, due to the low solubility of oxygen in molten Ag. With Ag–Sb alloy with added charcoal, the OCV at 973 K was 0.75 V, the potential associated with equilibrium between Sb and Sb₂O₃, due to the low solubility of oxygen in the Sb phase. The implications of these results for using molten Ag electrodes for direct carbon fuel cells are discussed.

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1. Introduction

Solid oxide fuel cells (SOFC) are based on oxygen ion conducting electrolytes, such as yttria-stabilized zirconia (YSZ), making it theoretically possible to electrochemically oxidize any combustible fuel, including solids like coal or biomass [1–7]. The primary limitation to using solid fuels in SOFCs is the difficulty in transferring the oxygen ions from the electrolyte interface to the surface of the fuel. Molten metal electrodes are promising as a way to overcome this limitation, since they can provide a pathway for oxygen transfer from the electrolyte to the solid carbon in a homogeneous molten phase. The desired reaction in the molten metal anode is that between the solid carbon and the dissolved oxygen in the metal, shown in Reaction (1).



The open-circuit voltage (OCV) for this reaction versus air depends on the form of the carbon, but will be approximately 1 V [8].

In earlier studies by our group [8,9], various molten metals were examined as anodes for the direct carbon reactions. With metals that have stable solid phase oxides at the operating temperature (e.g. Sn and In), the impedance of the cells became very high after briefly drawing current through the electrolyte due to formation of an oxide film at the electrolyte interface [9,10]. We showed that this problem could be avoided using molten Sb because both Sb and Sb₂O₃ are molten at reasonably low temperatures [8,9]; however, the OCV for cells with molten Sb anodes was only 0.75 V at 973 K, the potential established by equilibrium between Sb and Sb₂O₃. Even after prolonged electrolysis or when various carbonaceous fuels were mixed with the Sb, the OCV could not be increased. It appears that the solubility of oxygen in metallic Sb is very low [11,12], making it impossible to avoid formation of Sb₂O₃. Unfortunately, the presence of Sb₂O₃ at equilibrium establishes the cell potential at a value much

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lower than that which could be achieved if Reaction (1) were at equilibrium, resulting in a significant energy loss.

In order to establish equilibrium with Reaction (1) using a molten metal, it is desirable to have a high oxygen solubility in the metal phase and limited propensity for forming an oxide film over the electrolyte. Two metals that have been suggested for this application are copper [13,14] and silver [15–17]. Between these two, silver has the higher oxygen solubility [18] and the lower melting temperature ($T_{mp} = 1234$ K). Above its melting temperature, the Ag_2O phase is not stable, even at one atmosphere [19,20]. The solubility of oxygen in molten silver has been measured as a function of temperature and pressure and is known to depend on $P(O_2)^{1/2}$ [21].

The concept of using molten Ag as the anode for a direct carbon SOFC has been patented [17], but we are not aware of any experimental data showing how well it performs electrochemically. Therefore, in the work described in this paper, we set out to investigate the feasibility of using Ag for this application. We will demonstrate that a high OCV can be achieved using a molten Ag electrode with carbon fuels; however, the electrode impedances are very high, apparently due to limitations associated with oxygen transport to the fuel surface.

2. Experimental

The fuel cell studies were conducted using button cells made by methods that are described in detail in other papers [22–24]. The cells were constructed using a bilayer structure of the electrolyte material, YSZ (8 mol% Y_2O_3), with one side dense and the other porous. The dense electrolyte layer was 1 cm in diameter and 200 μm thick, while the porous layer was 0.67 cm in diameter and 50 μm thick. Composite cathodes were formed from the porous layer by infiltration of 40 wt% $La_{0.8}Sr_{0.2}FeO_3$ (LSF), using an aqueous solution of $La(NO_3)_3$, $Fe(NO_3)_3$, and $Sr(NO_3)_2$ in the proper molar ratios, and calcined to 1123 K [25,26].

The button cells were then attached to the end of an alumina tube using ceramic adhesive (Aremco, Ceramabond 552), after which the tube was mounted vertically in a tubular furnace. Two grams of Ag powder (99.9%, Alfa Aesar) were added to the anode side of the electrolyte with no additional treatment. Based on the density of silver metal and the inner diameter of the alumina tube, the metal layer above the electrolyte was roughly 0.4 cm thick. In some studies, solid carbon (charcoal from Supelco) was stirred together with the molten Ag to check its direct oxidation with dissolved oxygen. A platinum wire was attached to the cathode with platinum paste for electrical contact and the cell was treated at 1273 K for 30 min to secure adhesion. A single rhenium wire (0.5 mm diameter) was dipped into the molten metal for current collection on the anode side. Rhenium was chosen as a current collector because of its insolubility with silver and for its compatibility with Sb for other parts of the study.

The electrical measurements were performed using a Gamry Instruments Potentiostat at 1273 K. The cathode was exposed to the air, while the top of the tube holding the Ag was plugged with glass wool. The current densities were normalized to the external area of the cathode and the impedance spectra were performed galvanostatically in the frequency range from 300 kHz to 0.1 Hz with an a.c. perturbation of 1 mA. Because only one Re wire was used for current collection on the anode side, there is an ohmic contribution to the impedance spectra from this current collector.

3. Results and discussion

3.1. Pure silver anode

Before studying the effect of carbonaceous fuels, we examined the electrochemical performance of molten Ag in the absence of

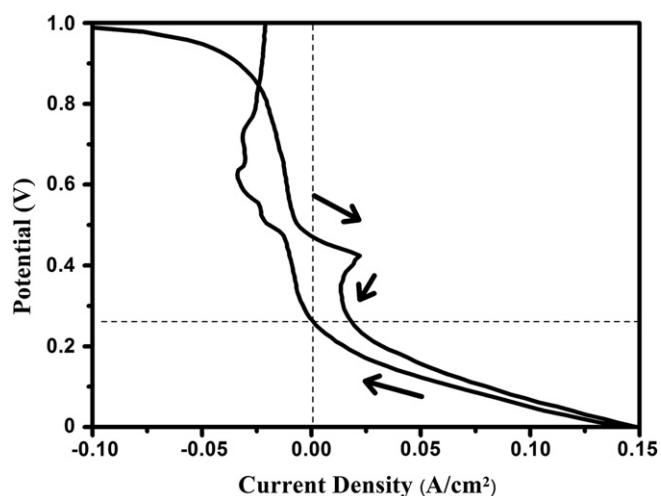


Fig. 1. Vi polarization curve for the system with pure Ag as anode obtained by ramping from 1 to 0 V and back at 10 mV s^{-1} .

carbon at 1273 K with no pretreatment. Fig. 1 shows the $V-i$ characteristics of such a cell. The current passing through the electrodes was measured while ramping the voltage from 1.0 to 0 V and back at 10 mV s^{-1} . Negative currents in this plot imply removal of oxygen from the anode compartment (i.e. the electrolysis regime) and the positive currents imply oxygen addition (i.e. the fuel cell regime). At the start of the downward ramp, there was a relatively large negative current, $\sim 100 \text{ mA cm}^{-2}$. This is likely associated with removal of residual oxygen in the molten Ag. In this particular experiment, the current becomes zero at a potential of 0.45 V, corresponding to a $P(O_2)$ of 10^{-8} atm. Since the Ag at the electrolyte interface must be in equilibrium with this $P(O_2)$ at OCV, it is possible to calculate the concentration of oxygen that is dissolved in the Ag at this point. Based on the reported, equilibrium solubilities of oxygen in Ag [21], the oxygen concentration is $\sim 4.4 \times 10^{-8} \text{ mol cm}^{-3}$.

With decreasing potential, positive currents were generated by the cell as O^{2-} flowed from the electrolyte into the Ag. Interestingly, there are two regions in the $V-i$ curve that can be clearly distinguished, one corresponding to potentials greater than 0.25 V and the other with potentials less than 0.25 V. Discussing the region from 0.45 to 0.25 V first, the $V-i$ curve exhibited a maximum current density of $\sim 25 \text{ mA cm}^{-2}$ at 0.42 V before decreasing with the cell potential. Qualitatively, the characteristics in this region were highly repeatable and were observed also at a ramp rate of 1 mV s^{-1} . Unlike the case with molten Sn or In [9,10], where a maximum in the current was also observed in $V-i$ curves measured using ramped potential due to formation of oxide films on the electrolyte, Ag_2O formation is not possible in this case.

With Ag, the reason for the declining current is that the driving potential for O^{2-} to pass through the electrolyte changes as oxygen is added to the Ag and the $P(O_2)$ in equilibrium with the dissolved oxygen increases. Therefore, measurement of the $V-i$ curve while ramping the potential is an intrinsically transient measurement. Indeed, integration of the current during the period where the cell potential goes from 0.45 to 0.25 V indicates that $2.5 \times 10^{-7} \text{ mol}$ of O^{2-} was added to the Ag. Assuming perfect mixing in the Ag phase, the oxygen concentration should be $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ when the potential reached 0.25 V. Using the equilibrium relationship for oxygen solubility as a function of $P(O_2)$, together with the Nernst equation, the equilibrium potential is expected to have decreased from 0.45 to 0.28 V.

Below 0.25 V, the $V-i$ relationship is nearly linear. The relatively constant slope in the region from 0.25 to 0 V strongly suggests that

the equilibrium potential for that part of the $V-i$ curve is not changing rapidly, as does the fact that the $V-i$ measurements made while ramping the potential back upward were not strongly different in this region. Interestingly, during the ramp back up to 1 V, the $V-i$ relationship crossed zero current at 0.25 V. Based on the coulombs of charge transferred to the Ag during the period in which oxygen was being added to the Ag (i.e. that period during which the potential was ramped from 0.45 to 0 V and back to 0.25 V.), approximately 3.2×10^{-6} mol of oxygen was added to the Ag, implying that the average oxygen concentration in the Ag would be 1.5×10^{-5} mol cm^{-3} . An equilibrium potential calculated from this value of concentration is 0.14 V, which is 100 mV lower than the observed value.

The fact that our measured OCV at this point in the experiment is higher than one would calculate based on the amount of oxygen that had been added implies that the oxygen concentration in the Ag at the electrolyte interface must be lower than the average concentration at this point in the measurement. The most likely explanation for this is that there is convection within the Ag anode that allows the more oxygen-rich material that is formed at the electrolyte interface to float to the Ag surface, causing the more oxygen-poor Ag to replace it. Indeed, convective flows due to density differences associated with dissolved oxygen in molten Ag have been reported previously [27].

Finally, it is also interesting to consider the electrolysis portion of the $V-i$ curve in Fig. 1, during which the potential is being ramped from 0.25 to 1.0 V. Above ~ 0.45 V, the current did not increase with potential. This is likely due to two effects. First, the oxygen concentration within the Ag at the electrolyte interface is being depleted, making electrolysis more difficult, even at higher potentials. Second, buoyancy forces keep the more oxygen-rich Ag well above the electrolyte interface. It is noteworthy that only about half as much oxygen was removed from the Ag during the electrolysis portion of this measurement as had been added during the fuel cell portion.

To better understand the electrochemical performance of the molten Ag anode, an impedance spectrum was measured for the cell in the flatter region of the $V-i$ curve, at fuel cell current density of 0.06 A cm^{-2} , while the cell potential was ~ 0.1 V. The results are shown in Fig. 2. The high frequency intercept with the real axis, 1.3 ohm cm^2 , has contributions from the ohmic losses in the cell, as well as the resistance of the rhenium current collector. The ohmic losses in the $200\text{-}\mu\text{m}$ thick, YSZ electrolyte are expected to be 0.25 ohm cm^2 based on the reported conductivity of YSZ at 1273 K,

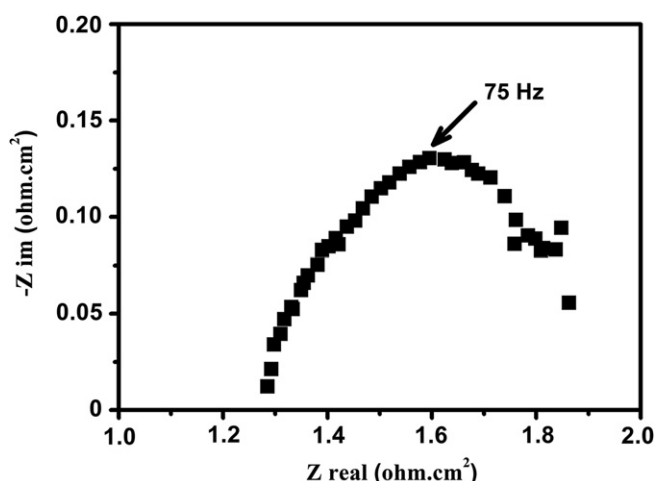


Fig. 2. Impedance data for cell using pure silver as anode, taken at 0.06 A cm^{-2} .

0.1475 S cm^{-1} [28]. The non-ohmic losses, given by the length of the arc between the high frequency and low frequency intercepts with real axis, were approximately 0.6 ohm cm^2 . Most of these losses are associated with the Ag anode, since the losses in the LSF-YSZ cathode at this temperature are almost certainly negligible.

3.2. Carbon in the molten silver electrode

Fig. 3 shows the $V-i$ characteristics of a cell having an anode that consisted of 0.5 g of charcoal and 2 g of Ag at 1273 K. The charcoal and Ag were mixed prior to heating the cell and were stirred using the Re current collector upon reaching the operating temperature. As in the case with pure Ag, the potential in Fig. 3 was ramped from OCV to 0 V and back at 1 mV s^{-1} , although there was no noticeable effect of current direction and ramp rate in this case. The equilibrium potential with the charcoal fuel was 1.12 V, which is close to the expected Nernst potential for carbon oxidation. Therefore, oxygen transport in the Ag is able to establish equilibrium with the carbon.

As in the case for pure Ag without charcoal, the $V-i$ relationship shows two distinct regions, corresponding to potentials below 0.25 V and those between 0.25 V and OCV. Because the shape and general characteristics below 0.25 V are similar to what was observed with pure Ag in Fig. 1, it is logical to assume that cell performance is dominated by the same processes in both cases, i.e. oxygen transport within the molten Ag. Therefore, cell performance is unlikely to be limited by reaction with carbon in this region. Although the high-potential region is more interesting for applications, the cell impedance, as estimated by the slope of the $V-i$ curve, was very high, $\sim 100 \text{ ohm cm}^2$ based on the slope of the $V-i$ curve, and the data again had a noisy appearance. Impedance spectra in this region demonstrated that the ohmic losses were 1.2 ohm cm^2 , the same value as that for the cell in Fig. 2, implying that most of the cell losses here are non-ohmic and associated with the Ag anode.

It is informative to consider the schematic shown in Fig. 4 in order to understand the likely causes for the poor electrode performance. Fig. 4a shows the overall cell configuration, while Fig. 4b focuses on the region near the electrolyte interface. From this diagram, it is clear that the overall anode reaction requires three rate processes that must operate in series: 1) O^{2-} transfer from the electrolyte to the molten Ag; 2) diffusion of dissolved oxygen from the electrolyte interface to the surface of the solid fuel; and 3) reaction of the dissolved oxygen with the solid fuel. It is also

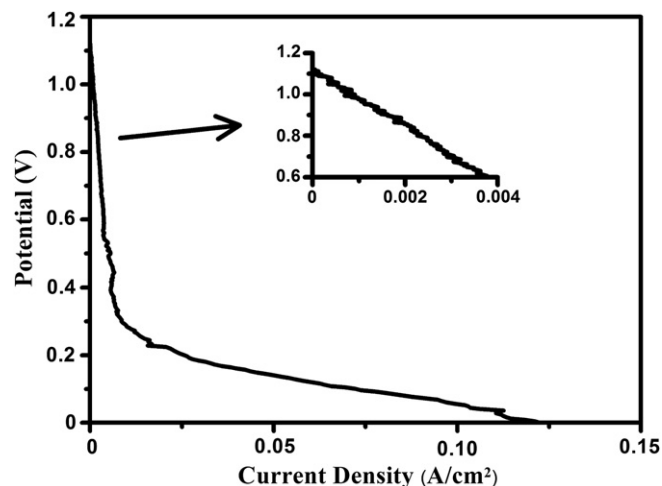


Fig. 3. $V-i$ polarization curve for the system with molten Ag anode with dispersed charcoal obtained by ramping from 1.2 to 0 V at 1 mV s^{-1} .

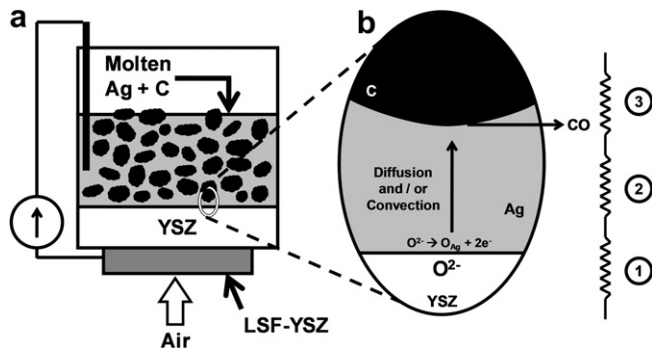


Fig. 4. A schematic of the electrochemical cell with solid carbon mixed with molten Ag anode (a) overall cell configuration, (b) mechanism of oxygen transfer in molten silver anode.

useful to consider that the oxygen concentration corresponding to a potential of 1.12 V in molten Ag at 1273 K is $4.4 \times 10^{-13} \text{ mol cm}^{-3}$.

Based on our previous measurements with molten Sb, we expect that rate process 1), O^{2-} transfer from the electrolyte to the molten metal, is likely to be facile so long as there is a potential driving force [8,9,29]. Of course, the driving force could be low if there is a significant amount of oxygen in the Ag, as the experiments with pure Ag have already indicated. Under the best circumstances, the potential at the electrolyte interface will be in equilibrium with the oxygen concentration in the Ag at this interface. Rate process 3), the reaction of dissolved oxygen with carbon, is difficult to estimate but should depend on the oxygen concentration. Again, under the best of circumstances, the reaction will be very fast so that the oxygen concentration at the carbon surface will be at equilibrium with Reaction (1).

Rate process 2), diffusion of dissolved oxygen, can be estimated if rate processes 1) and 3) are fast. Since the fuel particles will be at least $1 \mu\text{m}$ in size, it is reasonable to expect that the Ag film between the electrolyte and the carbon will be $\sim 1 \mu\text{m}$ on average, so that oxygen must diffuse at least this distance. Using the tabulated diffusivity of oxygen in Ag at 1273 K, $10^{-4} \text{ cm}^2 \text{ s}^{-1}$ [30], it is then possible to estimate the impedance associated with this step by calculating the oxygen flux associated with a given “overpotential.” For example, when the potential at the electrolyte interface is 1.0 V and the potential at the carbon surface is 1.12 V, the oxygen concentrations at the electrolyte interface and carbon surface will be $4.4 \times 10^{-12} \text{ mol cm}^{-3}$ and $4.4 \times 10^{-13} \text{ mol cm}^{-3}$. Based on Fick’s Law, $j = -D \text{ dc}/\text{dx}$, the calculated diffusive flux of oxygen between electrolyte interface and carbon surface is $4 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}$, which corresponds to a current density of $1.54 \times 10^{-6} \text{ A cm}^{-2}$. Therefore, at the overpotential of 0.12 V, the anode impedance would be on the order of 10^4 ohm cm^2 . Convective mixing, as discussed in the case with pure Ag, will decrease the actual electrode impedance and may be responsible for some of the “noise” in the data of Fig. 3; however, these calculations suggest that diffusion of oxygen within the electrode is likely to be limiting factor in controlling the performance of molten metal electrodes.

3.3. Carbon in Ag–Sb alloy anode

As noted above, it has previously been shown that reasonable performance can be achieved for direct utilization of carbon with a molten Sb electrode due to the fact that Sb_2O_3 is also molten [8,9]. However, the OCV for cells operating on Sb are always established by the Sb– Sb_2O_3 equilibrium, which is significantly lower than that which would be established for carbon oxidation. Since Sb and Ag form alloys, we examined this alloy for direct oxidation to determine whether the high solubility of oxygen in Ag might couple

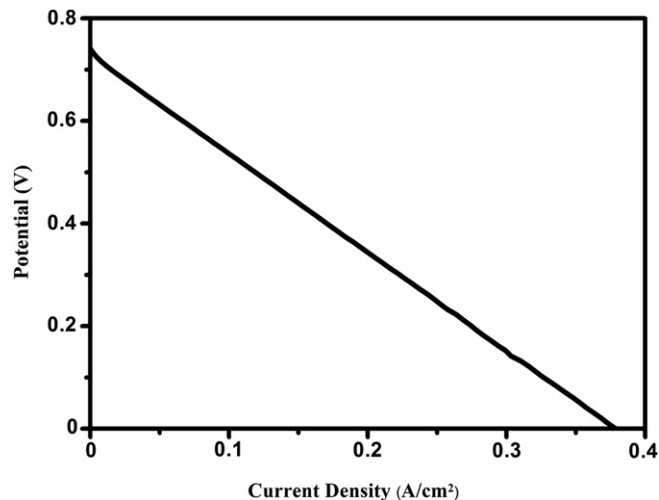


Fig. 5. Vi polarization curve for the system with Sb + Ag alloy (50 mol%, 2 g of Ag) as anode in the presence of 0.5 g of charcoal.

with the favorable features of Sb to improve the overall performance. Because Sb–Ag alloys melt at a much lower temperatures than Ag, it was also possible to operate the Ag–Sb cell at 973 K where the oxygen solubility in Ag should be much higher [21,30,31].

Fig. 5 shows the $V-i$ curve of a cell using 50 mol% Ag–Sb alloy (2 g of Sb, 99.5%, Alfa Aesar), mixed with carbon (0.5 g), at 973 K. Unfortunately, the data show that the OCV was still only 0.75 V, which is very close to the calculated value for the Sb– Sb_2O_3 equilibrium and much lower than that which would be expected for carbon oxidation. Indeed, other aspects of the performance of this cell were essentially identical to that for cells with only Sb as the anode. The $V-i$ relationship is a nearly straight line with a slope of $\sim 2 \text{ ohm cm}^2$. Since the cell had a 200- μm thick YSZ electrolyte (which alone would contribute an estimated resistance of 1.0 ohm cm^2) and only one current collector, the electrode losses must be relatively small, similar to what was observed for pure Sb electrodes [8,9] and much less than what was observed for the Ag electrodes operating at much higher temperatures. However, the main conclusion from Fig. 5 is that it is not possible to establish equilibrium for carbon oxidation with Sb-containing molten electrodes. It appears that the oxygen solubility in the metal is so low that Sb_2O_3 formation cannot be prevented.

4. Conclusions

The results here demonstrate direct oxidation of carbon in molten Ag anode, with open-circuit potentials that would be expected for equilibrium with carbon oxidation. However, analysis of the oxygen transfer to carbon dispersed in molten Ag suggests that there is a relatively large resistance associated with oxygen transport in the molten metal phase.

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