Short communication

Porous Ag–Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ cermets as anode materials for intermediate temperature solid oxide fuel cells using CO fuel

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A B S T R A C T

To study anode materials for intermediate temperature solid oxide fuel cells with Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (CSO) electrolyte using CO fuel, highly porous Ag–CSO cermets are prepared with MgO pore former and characterized. A single cell with 45Ag–CSO anode (Ag content: 45 wt%) is fabricated, tested, and compared with the similar cell with Cu–CeO$_2$–CSO anode. The 45Ag–CSO cermet shows high porosity (47%), high electrical conductivity (1254 S cm^{-1} at 923 K in CO), high activity (0.58 mmol$_{CO}$ min^{-1} g$_{Cat.}^{-1}$) and stability for CO oxidation at 923 K, and no carbon deposition. The single cell with 45Ag–CSO anode shows high open circuit voltage (1.13 V at 923 K and 1.11 V at 973 K with pure CO as the fuel and air as the oxidant), high maximum power density (MPD, 178.4 mW cm^{-2} at 923 K and 438.8 mW cm^{-2} at 973 K), and high stability (no apparent change in MPD over 100 h test at 973 K). This cell is much better in performance than the cell with Cu–CeO$_2$–CSO anode. Given that the CSO electrolyte is 0.385 mm thick, the performance is very encouraging. All the results suggest that the porous 45Ag–CSO cermet is an excellent anode material for ITSOFC with CSO electrolyte using CO fuel.

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1. Introduction

Solid oxide fuel cell (SOFC) has been intensively studied due to many of their advantages [1], including high efficiency in generating electricity, the lack of need for precious metals as the electrodes, and the use of non-hydrogen fuels, such as hydrocarbons, alcohols, CO and others. CO is considered to be a good candidate fuel since it can be generated by the gasification of chars with CO$_2$ at 973 K [2], and chars can be produced from plants or their wastes by carbonization [3]. Additionally, the process of generating CO also provides a means of recycling CO$_2$. For sustainable development, SOFC using CO fuel at intermediate temperature (IT, 773–973 K) is meaningful. However, very few studies [4–6], so far, have been reported on CO as the fuel of ITSOFC, and they were all limited to the cells with yttrium-stabilized zirconia (YSZ) electrolyte. For a single cell with YSZ electrolyte and Ni–YSZ anode, the maximum powder density (MPD) was found much lower for CO fuel than for wet hydrogen fuel [4–6]. For this fact, there are two explanations: (1) CO diffuses more difficultly than H$_2$ [4,5] and (2) unlike adsorbed H, adsorbed CO on Ni cannot spillover to YSZ surface and be oxidized thereby O^{2-} [6]. Recently, Pomfret et al. [7] found that, in comparison with dry hydrocarbon fuel, CO fuel had

much weaker carbon deposition on Ni–YSZ anode, and the tiny carbon deposit did not affect the performance of the fuel cell. They thought that the lower MPD for CO fuel might result mainly from the oxidation of Ni by O^{2-}, rather than from the carbon deposition. Costa-Nunes et al. [6] found that replacing Ni–YSZ anode with Cu–CeO$_2$–YSZ anode could increase the MPD of the fuel cell with CO fuel to the level of wet H$_2$ fuel; addition of Co to the Cu–CeO$_2$–YSZ anode could further increase the MPD for CO fuel to a level (370 mW cm^{-2} at 973 K) markedly higher than that for wet H$_2$ fuel (310 mW cm^{-2}, at 973 K). These results suggest that CO can be an excellent fuel for ITSOFC as long as a suitable anode and electrolyte are used.

YSZ electrolyte has low ionic conductivity in IT range, which results in low power output of ITSOFC. Therefore, it is necessary to replace YSZ with more conductive electrolytes, such as Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (CSO). With CSO electrolyte and Cu–CeO$_2$–CSO anode, the Gorte's group [8,9] had fabricated a single cell by firstly preparing "dense CSO/porous CSO" bilayer with graphite pore former, then applying cathode on the exposed surface of the dense CSO layer, and then impregnating the porous CSO with aqueous solution of copper and cerium nitrate, and annealing to form porous CuO–CeO$_2$–CSO, and finally reducing CuO–CeO$_2$–CSO at 973 K with H$_2$ to form porous Cu–CeO$_2$–CSO anode. Using this anode for dry butane oxidation, carbon deposition was avoided, but other problems were found: (1) the Cu was inactive to butane oxidation, CeO$_2$ must be added as catalyst; (2) the reduction step caused partial

reduction of the dense CSO, which led to low open circuit voltage (OCV) and low power output; and (3) the low porosity (∼50%) of the porous CSO led to the low contents of Cu (12.7 wt%) and CeO_2 (7.9 wt%), and in turn, the low electronic conductivity and low catalytic activity. Basically, these problems also exist for CO fuel. Therefore, new anode materials are required for ITSOFC with CO fuel.

This work investigates anode materials for ITSOFC with CSO electrolyte using CO fuel. To avoid the problems with Cu–CeO_2–CSO anode, highly porous Ag–CSO cermets were prepared by impregnating highly porous CSO disk with $AgNO_3$ aqueous solution, and then annealing in air at 773 K. The cermets were characterized as anode materials for ITSOFC using CO fuel. A single cell with Ag–CSO anode and CSO electrolyte was fabricated, tested, and compared with the similar single cell with Cu–CeO_2–CSO anode.

2. Experimental

2.1. Ag–CSO disk preparation

Ag–CSO porous disk was prepared by impregnating highly porous CSO disk (porosity: 68%) with $AgNO_3$ aqueous solution, and calcining in air at 773 K for 4 h. The resulting disk sample was termed as xAg–CSO, where x represents the wt% of Ag over the total weight of the disk. Following our previous method [10], the highly porous CSO disk was prepared by selectively leaching MgO from CSO–MgO disk with acetic acid solution (60 vol.%) at 353 K. The CSO–MgO disk was prepared by uniaxially pressing the mixed powder of CSO and MgO (MgO/CSO = 3.3, molar ratio) in a stainless steel die (i.d. 13 mm) under 750 MPa, and then sintering at 1773 K for 5 h. The CSO powder was prepared with a sol–gel method following the procedure described elsewhere [11]. The MgO powder was prepared by calcining $Mg(NO_3)_2 \cdot 6H_2O$ at 773 K for 5 h.

2.2. Ag–CSO disk characterization

2.2.1. Porosity, structure, and conductivity

The porosity of the disk samples was measured with a mercury porosimetry (Pore Master 33). The crystal structures of the disk samples were identified at room temperature using an X-ray diffractometer (Rigaku/MAX-II, Cu Kα radiation). The electrical conductivities of the disk samples in CO were measured at 923 K with four-probe DC method (Autolab).

2.2.2. Catalytic activity and carbon deposition

The disk samples (xAg–CSO) with diameter of 10.75 mm and thickness of 1.0 mm were crushed into 40–60 mesh, and tested at different temperatures (373–973 K) for CO oxidation in a flow reactor (quartz tube, i.d. 7 mm) at atmospheric pressure. The space velocity was 34,682 h^{-1}. The gas-mixture fed into the reactor contained air (10.74%), CO (4.54%), and N_2 (84.72%). The effluent of the reactor was analyzed with a Gas Chromatograph (Shimadzu GC-9A) with a carbon molecular sieve column and a thermal conductive detector. The reaction rate of CO was calculated using the following equation:

$$\text{rate} (\text{mol min}^{-1}\,\text{g}^{-1})$$
$$= \frac{\text{flow rate of CO} (4.54\,\text{mL min}^{-1}) \times \text{CO conversion}}{22,400 (\text{mL mol}^{-1}) \times \text{catalyst wt} (\text{g})}$$

Carbon deposition on the samples was tested by measuring the total carbon content ($CO + CO_2$) in the effluent of the reactor as a function of reaction temperature. It was also tested by measuring the weight-increment of the samples after being treated with

pure CO. In this weight measurement, the sample temperature was ramped to 973 K in flowing He, exposed to flowing pure CO for 10 h, and then cooled in flowing He.

2.3. Single cell fabrication and test

The single cell was 1.1 cm diameter and contained a dense CSO electrolyte layer (0.385 mm thick) attached to a porous CSO layer. The porous layer was used as the anode (0.153 mm thick) and was impregnated with Ag. A CSO–lanthanum strontium cobalt ferrite (LSCF) layer was pasted onto the exposed surface of the dense electrolyte to form the cathode (0.012 mm thick). The dense CSO/porous CSO bilayer disk was fabricated by uniaxially pressing a bilayer of pure CSO powder and CSO powder containing MgO pore former, and then annealing in air at 1773 K for 5 h, and finally leaching with acetic acid solution (60 vol.%) at 358 K to remove the MgO and leave a porous layer of CSO supported on the dense CSO electrolyte. Porosity measurements showed that the porosity of the porous layer was 63%. Composition analysis showed that the residue of MgO in the porous layer was less than 3 wt%. A 50:50 wt% mixture of CSO and LSCF (Nextech) was pasted onto the exposed surface of the electrolyte and fired in air at 1273 K for 1 h to form the cathode. The porous CSO anode layer was then impregnated with aqueous solution of $AgNO_3$. The nitrate salt was decomposed to form metal Ag by heating in air at 773 K for 4 h. The content of Ag in the anode was 45 wt%. Therefore, the anode was termed as 45Ag–CSO.

Silver current collectors were attached to the cathode and anode using Pt and Ag paste, respectively. The fuel-cell disk was then attached to an alumina-support tube and sealed using high temperature ceramic cement (Aremco; Ceramabond 571). The active area of the anode and cathode was 0.5 cm^2.

For comparison, a single cell with the same electrolyte (0.382 mm thick) and cathode (0.010 mm thick) but using Cu–CeO_2–CSO anode (composition: Cu 12.7 wt%, CeO_2 7.9 wt%, and porous CSO 79.4 wt%; thickness: 0.155 mm) was also fabricated in the same way except that $AgNO_3$ was replaced with $Cu(NO_3)_2$ and $Ce(NO_3)_4$, and a reduction step (H_2 20 mL min^{-1}, 973 K, 2 h) was applied to reduce CuO to Cu.

Pure CO (99.999%) was supplied to the anode as the fuel at a pressure of 0.1 MPa and a flow rate of 150 mL min^{-1}. The cathode was exposed to air. The CO conversion at 923–973 K within the cell was about 5%. Current–voltage (I–V) curve, current–power curve (I–P), and runtime–power curve (t–P) were obtained using computer-controlled electrochemical equipment (Autolab).

3. Results and discussion

We had found in our previous studies [10,11] that the synthesized CSO powder was a single phase of ceria-based solid solution. The CSO dense disk sintered at 1773 K for 5 h was still a single phase of ceria-based solid solution, and had a relative density of 93% and an ionic conductivity of 0.025 S cm^{-1} at 923 K, indicating that the sintering condition was suitable for preparing dense CSO ceramics with high ionic conductivity. The porous CSO disk synthesized with MgO pore former had a porosity of 68%, much higher than that (50%) reported in Ref. [8] using graphite pore former. This porous disk still had an acceptable strength and ionic conductivity (0.003 S cm^{-1}, at 923 K); therefore, it could be used further to prepare porous xAg–CSO cermets.

Fig. 1 shows the porosity of the xAg–CSO disk as a function of Ag content (x). The porosity decreased with x almost linearly, and at x = 45%, reached about 47%, much higher than that (about 32%) of the Cu–CeO_2–CSO anode prepared following the same procedure described in Refs. [8,9] using graphite pore former. Fig. 2 shows the XRD patterns of xAg–CSO cermets. Only metal Ag and
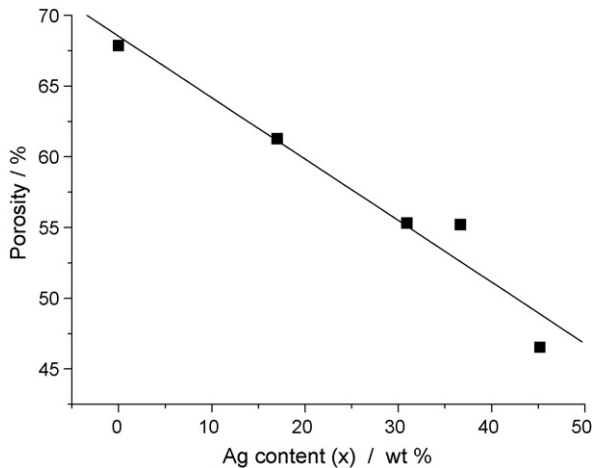
Fig. 1. The porosity of the xAg–CSO disk samples as a function of Ag content (x).
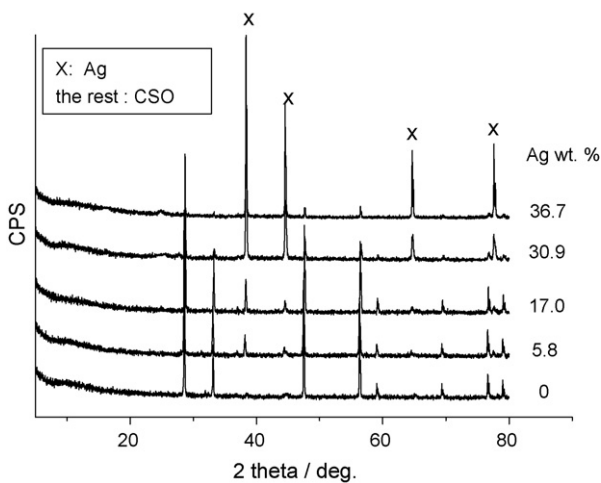

Fig. 2. XRD patterns of xAg–CSO disk samples with different Ag content (x).

CSO phases were observed in the Ag-containing samples. The XRD peaks increased with x for Ag phase but decreased for CSO phase. When $x \geq 36.7$ wt%, mainly Ag phase was observed, indicating that most of the CSO surface was covered by Ag.
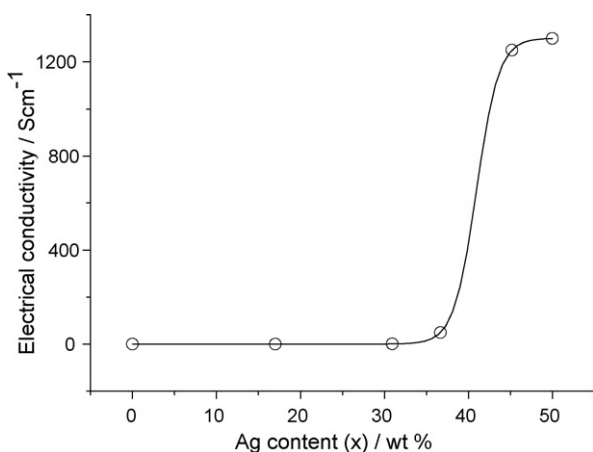

Fig. 3. Effect of Ag content (x) on the electrical conductivity of the xAg–CSO disk samples in CO and at 923 K.
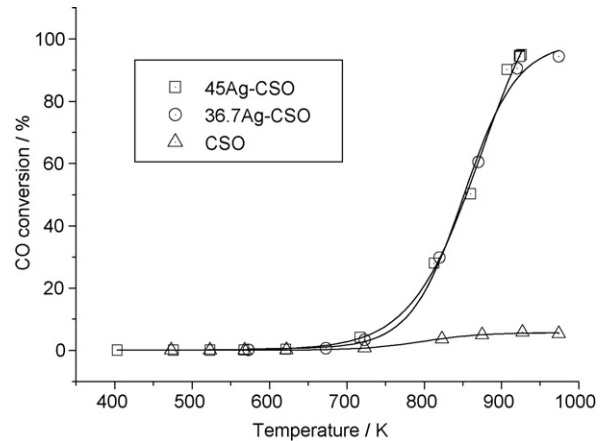

Fig. 4. CO conversion of the reaction of CO oxidation on xAg–CSO catalysts at atmospheric pressure as a function of reaction temperature (reactor inlet gas-mixture: CO 4.54%, air 10.74%, and N_2 84.72%. GHSV = 34,663 h^{-1}).

Fig. 3 shows the electrical conductivity of the xAg–CSO disks in CO and at 923 K as a function of Ag content (x). The function was like an S-shaped curve. A steep rise in electrical conductivity (from 0.003 S cm^{-1} to 1254 S cm^{-1}) emerged at $x = 35$–45 wt%, which was caused by a switch in controlling mechanism from ionic conduction of CSO to electronic conduction of Ag. When x rose to 45 wt%, the conductivity reached 1254 S cm^{-1}, much higher than that (100–300 S cm^{-1}) reported in Ref. [12] for Ni-based anode.

Fig. 4 shows the catalytic activities of three xAg–CSO samples for CO oxidation as a function of reaction temperature. For all the samples, the reaction started at about 723 K, but with temperature increasing, the activity increased much more rapidly for the Ag-containing samples than for the pure CSO, indicating that Ag was much more active than CSO. Consistent with the XRD (Fig. 2) and conductivity (Fig. 3) results, the two Ag-containing samples showed close activities over the whole temperature range. When x rose to 36.7 wt%, a continuous phase of Ag might form gradually and cover most of the CSO surface. Therefore, Ag was observed the main phase in the XRD pattern (Fig. 2), and the conductivity rose steeply (Fig. 3). Further increase of the Ag content from 36.7 wt% to 45 wt% might not markedly increase the number of active Ag sites on the surface, therefore, the activities of the two Ag-containing samples had no marked difference. At 923 K, the CO conversion of the two Ag-containing samples reached about 95%, equivalent to a reaction rate of 0.58 mmol$_{CO}$ min^{-1} g$_{Cat.}^{-1}$.

The stabilities of the three samples in Fig. 4 were tested at 923 K by recording CO conversion as a function of reaction time (Fig. 5). For all the samples, the CO conversion did not change apparently with reaction time, indicating that the samples were all quite stable. These samples were also tested for carbon deposition by analyzing the total carbons from the effluent of the reactor as a function of reaction temperature (Fig. 6). The total carbon did not change apparently with temperature, indicating that no carbon deposition occurred, or at least, the carbon deposit was undetectable. This measurement has an uncertainty of about 0.5 ppm, implying that if carbon deposition rate is less than 1.47 μg h^{-1}, the carbon deposit will not be observed. The carbon deposition was also tested by measuring the weight-increment of the sample after being treated with pure CO at 973 K for 10 h. We found that the weight-increment was also negligible. Ag and ceria had been found to be inactive for CO decomposition [13,14,16,17], but active for carbon oxidation [15]. Therefore, it is believable that carbon deposition on Ag–CSO cermet is at least negligible.
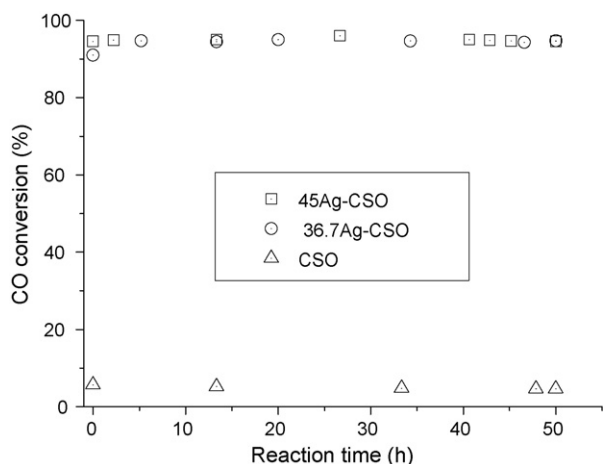
Fig. 5. CO conversion of the reaction of CO oxidation on xAg–CSO catalysts at atmospheric pressure and 923 K as a function of reaction time (reactor inlet gas-mixture: CO 4.54%, air 10.74%, and N_2 84.72%. GHSV = 34,663 h^{-1}).

We noticed that, for CO oxidation at 923 K, 45Ag–CSO sample was stable and no carbon deposition; it had high porosity (47.3%), high electrical conductivity (1254 S cm^{-1}), and high activity. In mechanism, CO oxidation by O_2 is close to that by O^{2-}; therefore, 45Ag–CSO sample is also possible to have high electro-catalytic activity for CO oxidation by O^{2-}. All the properties of the 45Ag–CSO sample suggest that it might be an excellent anode material for ITSOFC using CO fuel.

Fig. 7 shows the performance of the single cell with 45Ag–CSO anode in comparison to that with Cu–CeO$_2$–CSO anode. The cell with 45Ag–CSO anode had an OCV of 1.130 V at 923 K and 1.110 V at 973 K, and a MPD of 178.4 mW cm^{-2} at 923 K and 438.8 mW cm^{-2} at 973 K; whereas, the similar cell with Cu–CeO$_2$–CSO anode had an OCV of 0.907 V at 923 K and 0.861 V at 973 K, and a MPD of 134.8 mW cm^{-2} at 923 K and 237.5 mW cm^{-2} at 973 K.

Usually CSO electrolyte has tiny electronic conductivity which partially leads to the short-circuiting, and in turn leads to the decrease of the OCV [1]. Therefore, the measured OCV values (Fig. 7) were lower than the theoretical values (1.114 V at 973 K and 1.132 V at 923 K). Since the electronic conductivity of CSO increased with
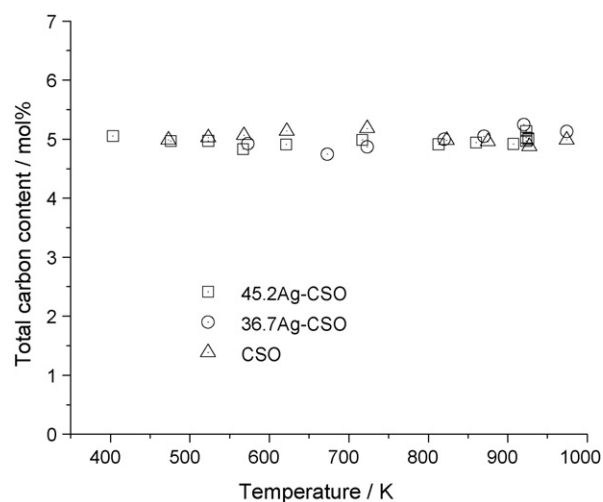

Fig. 6. The total carbon content in the effluent of the reactor for the reaction of CO oxidation on xAg–CSO catalysts at atmospheric pressure as a function of reaction temperature (reactor inlet gas-mixture: CO 4.54%, air 10.74%, and N_2 84.72%. GHSV = 34,663 h^{-1}).
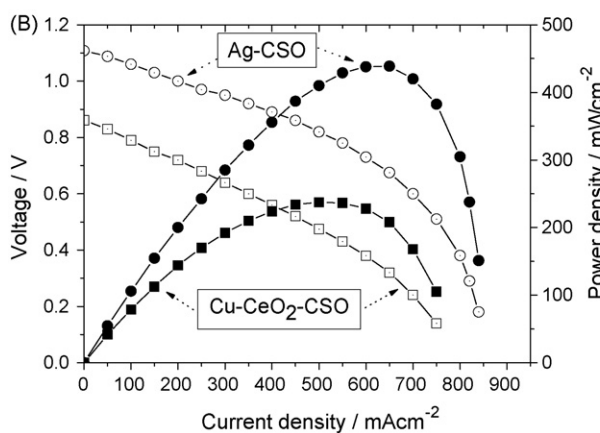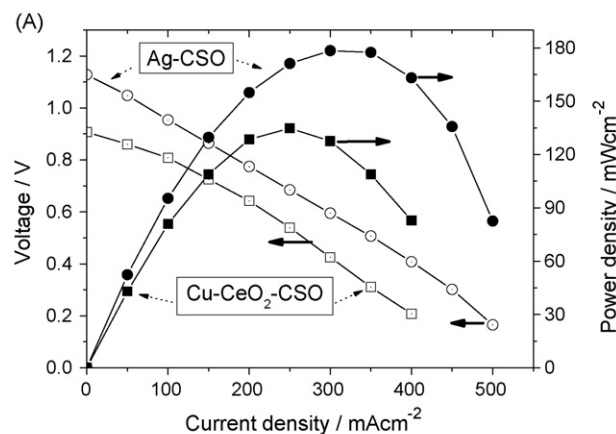

Fig. 7. The voltage and power density of the single cells with the anode of 45Ag–CSO and Cu–CeO$_2$–CSO as the functions of current density (Panel A: 923 K and Panel B: 973 K).

temperature, the OCV of the cells at higher temperature was a little lower. The single cell with Cu–CeO$_2$–CSO anode required the H$_2$ reduction step for activation, which led to the partial reduction of CSO electrolyte layer, and in turn, the increase of electronic conductivity, and the decrease of OCV. The single cell with Ag–CSO anode did not require H$_2$ reduction; therefore, it had higher OCV (1.110 V at 973 K) than the cell with Cu–CeO$_2$–CSO anode (0.861 V at 973 K). However, the OCV (1.110 V at 973 K) of the cell with Ag–CSO anode was still slightly lower than the theoretical value (1.114 V at 973 K). This might be caused by slightly partial reduction of CSO by CO. Considering H$_2$ defuses more rapidly than CO [4,5], CO might reduce CSO much more weakly than H$_2$. The effect of H$_2$ treatment on the performance of the cell with Ag–CSO anode was also tested. After the treatment with H$_2$ at 973 K for 2 h, the OCV of the cell with CO fuel decreased from 1.110 V (at 973 K) to 0.901 V (at 973 K), indicating that H$_2$ has a much stronger reduction effect than CO on the CSO electrolyte.

At higher temperature, the CSO electrolyte had higher ionic conductivity, i.e. lower resistance for O^{2-} conduction; the anode and cathode had lower resistance and impedance; therefore, the single cell had lower inner resistance, and consequently higher MPD. Since Ag–CSO anode might have much higher electronic conductivity and even higher electro-catalytic activity than Cu–CeO$_2$–CSO anode, the single cell with Ag–CSO anode had higher MPD than that with Cu–CeO$_2$–CSO anode.

The stability of the single cell with 45Ag–CSO anode was tested at 923 K and 973 K over 100 h (Fig. 8). The MPD did not change apparently with runtime, indicating that the anode is quite sta-
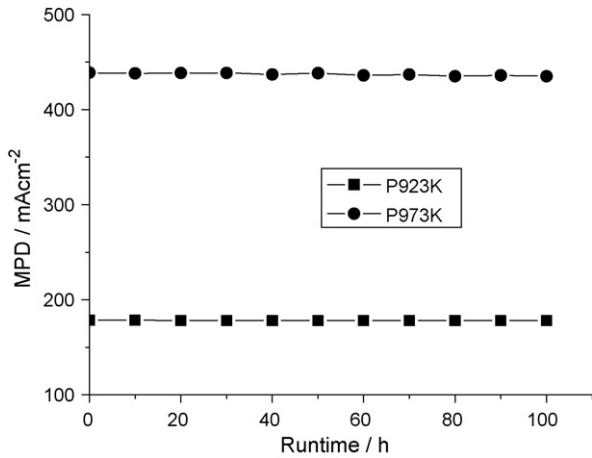
Fig. 8. The maximum power density (MPD) of the single cell with 45Ag–CSO anode as a function of runtime.

ble, and has no such problems as the evaporation of Ag and the deposition of carbon on Ag. This result is supported by the data in Figs. 5 and 6, and also the data in Refs. [13–18] where Ag evaporation at 973 K from Ag-based cathode was found negligible [18]; in addition, Ag and ceria were both found active for carbon oxidation [15], but inactive for CO decomposition [13,14,16,17].

4. Conclusions

Highly porous Ag–CSO cermets were prepared and characterized. A single cell with CSO electrolyte and Ag–CSO anode was fabricated, tested, and compared with the similar cell with Cu–CeO$_2$–CSO anode. The 45Ag–CSO cermet showed high porosity (47%), high electrical conductivity ($\approx$1254 S cm^{-1} at 923 K in CO), high activity ($\approx$ 0.58 mmol$_{CO}$ min^{-1} g$_{Cat.}^{-1}$) and stability for CO oxidation at 923 K, and no carbon deposition. The single cell with 45Ag–CSO anode showed high OCV (1.13 V at 923 K and 1.11 V at 973 K), high MPD (178.4 mW cm^{-2} at 923 K and 438.8 mW cm^{-2} at 973 K), and high stability at 923–973 K. This cell is much better in performance than the similar cell with Cu–CeO$_2$–CSO anode. This performance is very encouraging given that the CSO electrolyte is 0.385 mm thick. All the results suggest that the porous 45Ag–CSO cermet is an excellent anode material for ITSOFC with CSO electrolyte using CO fuel.

Acknowledgement

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