Short communication

A high performance direct ammonia fuel cell using a mixed ionic and electronic conducting anode

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Abstract

A high performance direct ammonia fuel cell incorporating a doubly doped barium cerate electrolyte and a novel cermet anode consisting of europium doped barium cerate, a mixed ionic and electronic solid electrolyte, and Ni was studied. The catalytic activity of the cermet anodes was superior to that of Pt catalysts. The *I–V* and power density data suggest that the direct ammonia fuel cell could be operated at temperatures as low as 450 °C. The fuel cell was operated with ammonia as fuel in excess of 500 h without significant deterioration in performance.
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1. Introduction

Hydrogen fuel cells represent a promising alternative energy producing technology. If widely implemented in the transportation and stationary power generation sectors they could significantly contribute to reduction of greenhouse gas emissions (GHG). The only waste product generated by fuel cells using hydrogen as fuel is water. The advent of a hydrogen economy would allow the widespread use of hydrogen fuel cells. However, several technological challenges related to hydrogen production, transportation and storage infrastructure have yet to be resolved.

Ammonia is an inorganic hydrogen carrier which can be easily stored and is one of the highest volume chemicals produced worldwide [1]. Assuming that fossil fuels are not used as the feed stock then ammonia is a carbon-free fuel and contributes to reduced GHG emissions. However, if fossil fuels are used to synthesize ammonia then the carbon dioxide generated can be separated and captured. One distinct advantage of hydrogen fuel cells incorporating a proton conducting electrolyte is that water is formed at the cathode, thus the fuel

at the anode remains pure thereby eliminating the need for recirculation. The use of ammonia also avoids the deleterious coking problem normally encountered when hydrocarbons are used as fuel. Ammonia as fuel in intermediate temperature fuel cells using yttria stabilized zirconia oxygen ion conducting electrolyte [2] and gadolinium doped barium cerate proton conducting electrolyte [3] have been reported. Subsequent to these initial reports numerous publications on ammonia fuel cells have been published [4–10]. These reports indicate that ammonia is a viable fuel, particularly for stationary fuel cell applications.

In this paper the operation of a direct ammonia fuel cell utilizing a gadolinium and praseodymium doped barium cerate ($BaCe_{0.8}Gd_{0.15}Pr_{0.05}O_3$, BCGP) solid electrolyte is reported. The anode consisted of a mixed ionic and electronic conducting europium doped barium cerate ($BaCe_{0.85}Eu_{0.15}O_3$, BCE) and Ni cermet. BCE was previously shown to be suitable for hydrogen pumping applications [11] and also shown to be stable in ammonia [7]. The presence of significant electronic conduction in BCE suggests that it may perform well as a anode. The ammonia cracking characteristics of the Ni–BCE cermet anode are reported. The performance characteristics of electrolyte supported monolithic fuel cells using BCGP solid electrolyte and Ni–BCE cermet anode using both hydrogen and ammonia, separately, as fuel are presented.

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2. Experimental

BCGP powders were prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of high purity oxide powders ($BaCO_3$, CeO_2, Gd_2O_3 and Pr_6O_{11}) were ball milled in isopropyl alcohol for 24 h. The dried powders were subsequently calcined at 1350 °C in air for 10 h. The calcined powder was mixed with a 15% polyvinyl alcohol solution and uniaxially pressed at 65 MPa into approximately 3 cm diameter and 2 mm thick pellets. The samples were subsequently isostatically pressed at 275 MPa. The discs were then sintered at 1600 °C in air for 10 h and ground and polished to approximately 1 mm thickness.

BCE powders were also prepared by conventional solid-state synthesis techniques. Appropriate stoichiometric ratios of high purity oxide powders ($BaCO_3$, CeO_2 and Eu_2O_3) were ball milled in isopropyl alcohol for 24 h. The dried powders were calcined at 1350 °C in air for 10 h. The calcined BCE powder was mixed with NiO in various weight percent (wt%) ratios. The cermet anode powder was ground, mixed and then ball milled in isopropyl alcohol for 24 h. Solvents were evaporated and the dried powders were calcined at 1400 °C in air for 5 h.

Planar single element fuel cells were fabricated utilizing Engelhard platinum ink A-4338 for the cathode and Ni–BCE cermet anode. The calcined NiO–BCE cermet anode powder was ground and mixed with an ink vehicle (Fuel Cell Materials, USA) and slurry-coated onto the BCGP electrolyte. The coated disc was fired at 1400 °C for 2 h, with heating and cooling rates of 5 °C min^{-1}. The Pt cathode electrodes were air dried and then fired at 1000 °C for 1 h, with heating and cooling rates of 5 °C min^{-1}.

During fuel cell operation a gas flow of 50 cm^3 min^{-1} of hydrogen or ammonia was supplied at the anode while 50 cm^3 min^{-1} of air was maintained at the cathode. The fuel cell was heated to 600 °C at a ramp of 3 °C min^{-1}. The exhaust gas compositions were analyzed with an Agilent 3000A micro-gas chromatograph (µGC) to determine leftover ammonia at the anode.

Ni–BCE powders were evaluated as ammonia cracking catalysts in a fixed bed quartz reactor (5 mm i.d.) at 6000 h^{-1} gas hourly space velocity (GHSV). An alumina well was inserted through the bottom of the reactor to seat a thermocouple directly below the catalyst bed. The Ni–BCE powder was reduced in H_2 at 700 °C for 1 h. The reactor was cooled to reaction temperature where a flow of 50 cm^3 min^{-1} of ammonia was introduced. Outlet gas compositions were analyzed by an Agilent 3000A micro-gas chromatograph (µGC). Ammonia conversions were measured between 400 and 650 °C. Ni–BCE powders with Ni concentrations from 1 to 50 wt% were compared.

A Hitachi S-3400N scanning electron microscope (SEM) was used to observe the microstructure. Elemental maps were obtained by energy dispersive spectroscopy (EDS) using an Oxford INCA 450 equipped with a Si(Li) detector.
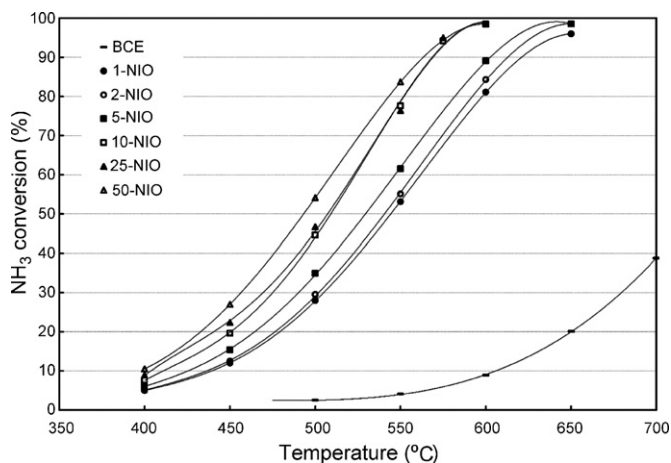

Fig. 1. Ammonia conversion as a function of temperature for various Ni–BCE cermet compositions (1-NiO refers to a Ni–BCE cermet sample with 1 wt% NiO and 99 wt% BCE; 2-NiO refers to a Ni–BCE cermet sample with 2 wt% NiO and 98 wt% BCE, etc.).

3. Results and discussion

The high cost of platinum requires that alternative electrode materials be found for the anode and cathode. The use of a cermet anode consisting of a nickel–BCE composite anode electrode is reported. Nickel is a well known catalyst at intermediate temperatures. BCE is a mixed conducting electrolyte, conducts both protons and electrons [11], and was shown to perform well with ammonia as fuel [7]. The catalytic behaviour of NiO–BCE composite cermets as a function of temperature was studied. Fig. 1 shows the percent of ammonia conversion as a function of temperature for different NiO–BCE cermet compositions. The data show that the incorporation of nickel greatly enhances the ammonia conversion. The data for BCE is included and shows the BCE does not have any significant catalytic activity. These data also show that nickel loading as low as 1 wt% completely decomposes ammonia at 650 °C.

Fig. 2 shows the ammonia conversion as a function of NiO loading on BCE at various temperatures. The reference sample is a 1 wt% Pt on SiO_2 catalyst. The data show that the NiO–BCE
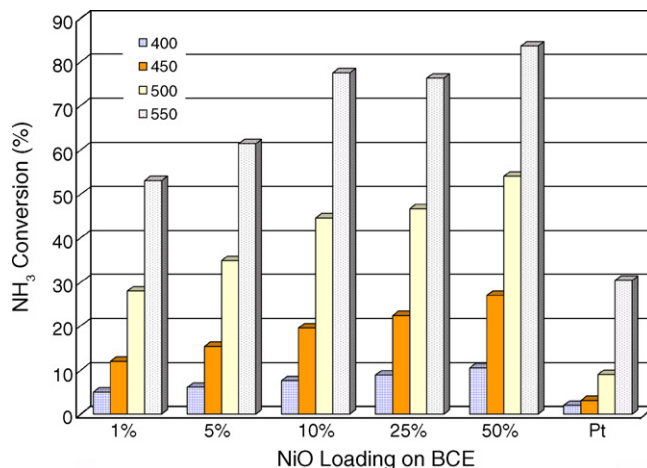

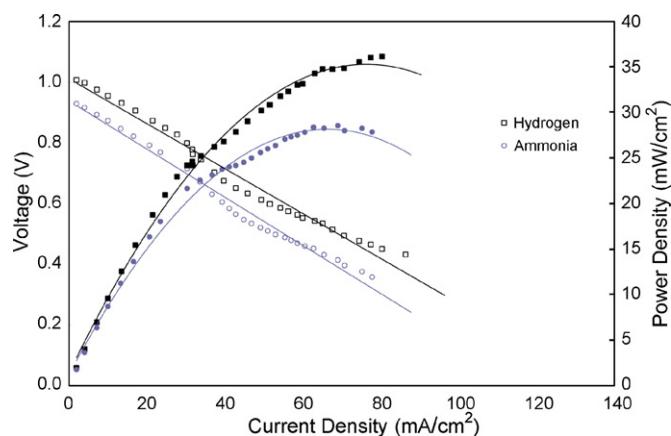Fig. 2. Ammonia conversion as a function of NiO loading on BCE. The platinum sample is a 1 wt% Pt on SiO_2 catalyst.

Fig. 3. I–V data for electrolyte supported NiO–BCE/BCGP/Pt cell assembly at 600 °C.

cermet is more efficient at converting ammonia than platinum, at all temperatures studied. The data shows that this cermet anode has considerable catalytic activity even at temperatures as low as 450 °C.

A monolithic electrolyte supported fuel cell incorporating a NiO–BCE (60 wt% NiO–40 wt% BCE) anode on a BCGP electrolyte with platinum cathode was constructed. The performance characteristics of this monolithic fuel cell using ammonia and hydrogen, separately, as fuel were studied. Fig. 3 shows I–V and power density data for the electrolyte supported fuel cell at 600 °C. The linear I–V data indicate little if any polarization at the electrodes. The data show that the fuel cell performed well in both hydrogen and ammonia. The data in ammonia while similar to those collected in hydrogen are, however, slightly lower. This behaviour can be attributed, in part, to the lower partial pressure of hydrogen due to the presence of nitrogen.

Fig. 4 shows the power density data for a monolithic BCGP electrolyte supported fuel cell. The data compares the performance of a fuel cell with a Pt anode and one with NiO–BCE (60/40 wt%) anode. The cathode was Pt in both cases. The data were collected using ammonia as fuel and the cells were operated at 600 °C. Clearly, the fuel cell with the NiO–BCE cermet anode

outperforms the fuel cell with a Pt anode. This data suggests that the NiO–BCE anode is a viable alternative to Pt. Fig. 5 shows the amount of unconverted ammonia at the anode outlet as a function of temperature. The NiO–BCE anode is more effective at converting ammonia than the Pt anode. These data show that a fuel cell incorporating a NiO–BCE anode can be operated at temperatures as low as 450 °C, albeit with some deterioration in conversion efficiency.

Fig. 6 shows the power density for a NiO–BCE/BCGP/Pt fuel cell operating at various temperatures. The data were collected using ammonia as fuel. The data show that while the power density decreases with temperature, as expected, the values are still quite high. These data indicate that the operating temperature of the fuel cell can be reduced without significant decrease in performance. Operation at lower temperature would increase the operating lifetime of the fuel cell.

Fig. 7 shows the voltage output of a NiO–BCE/BCGP/Pt fuel cell versus time. The data show that the fuel cell was very stable for extended periods of time with little degradation in performance. The fuel cell was tested in excess of 500 h. To the best of our knowledge this is the longest a fuel cell has been tested with ammonia as fuel. The dramatic decrease in voltage after

Fig. 5. Unconverted ammonia at the anode outlet as a function of cell operating temperature. BCGP electrolytes with Pt cathodes were used.
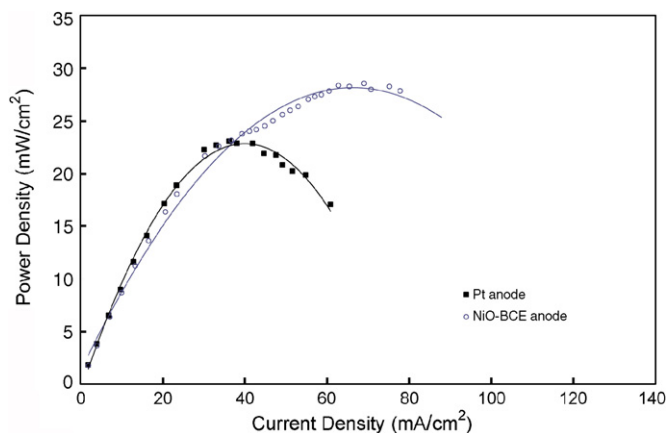

Fig. 4. Power density data for BCGP electrolyte cells comparing Pt and NiO–BCE anodes. Cells operating at 600 °C under ammonia fuel with Pt cathodes.
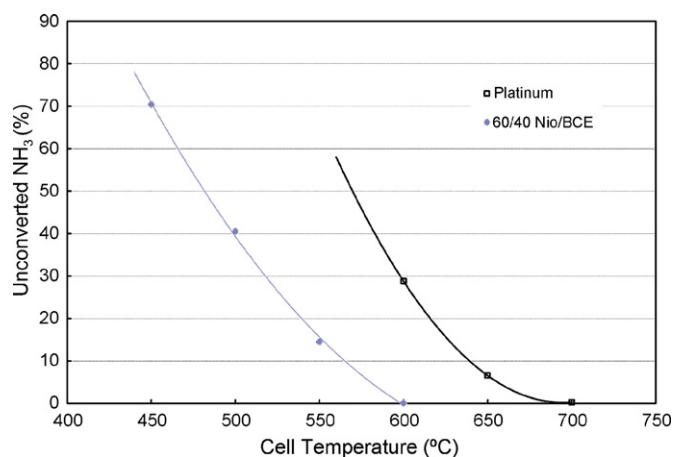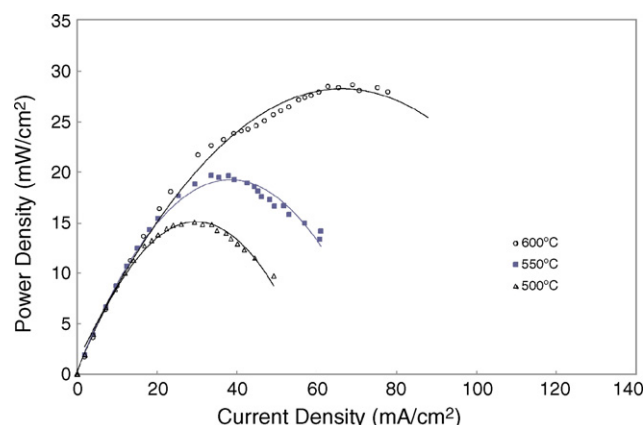

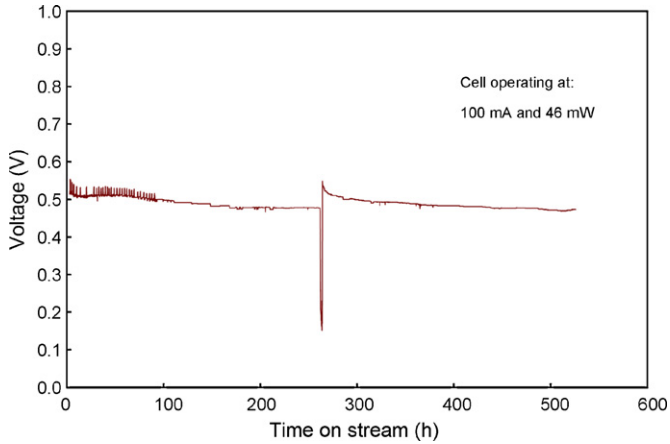Fig. 6. Power density data for electrolyte supported NiO–BCE/BCGP/Pt cell assembly operating at various temperatures.

Fig. 7. Voltage versus time data for NiO–BCE/BCGP/Pt cell assembly operating near peak power output under ammonia at 600 °C.

Fig. 8. SEM micrograph of sintered (1400 °C) BCGP electrolyte surface coated on NiO–BCE anode.

approximately 250 h of operation was due to the loss of air at the cathode. The air supply was restored and the output voltage of the cell recovered to the original value. This behaviour shows that the cell assembly is quite robust and can tolerate extreme operating conditions without significant performance degradation.
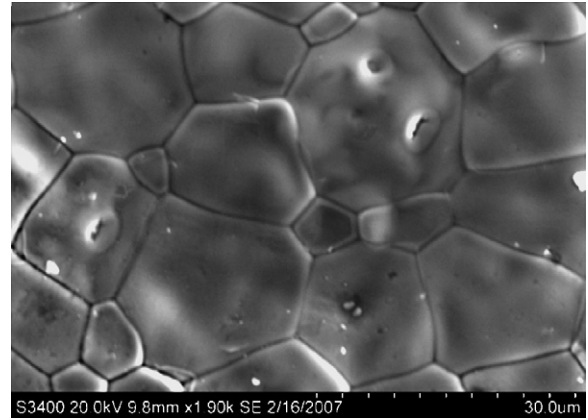
The preceding data were collected on a monolithic electrolyte supported fuel cell. The thickness of the electrolyte was approximately 1 mm thick. In order to increase the performance of the fuel cell an anode supported structure is desirable. This cell architecture would allow the thickness of the electrolyte to be reduced resulting in a lower overall ohmic resistance which
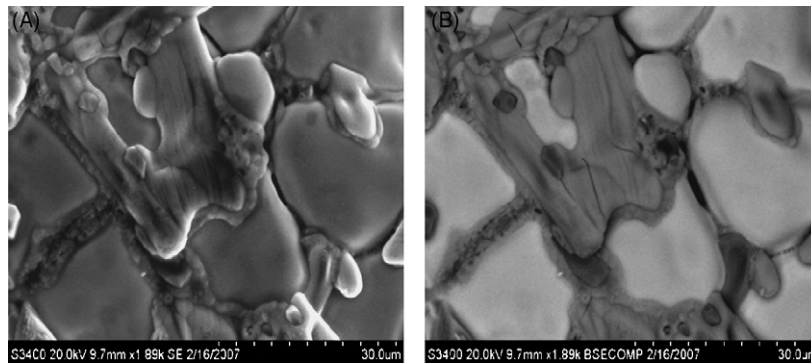

Fig. 9. SEM micrograph of sintered (1400 °C) NiO–BCE anode surface. (A) Secondary electron mode. (B) Backscattering-electron mode.
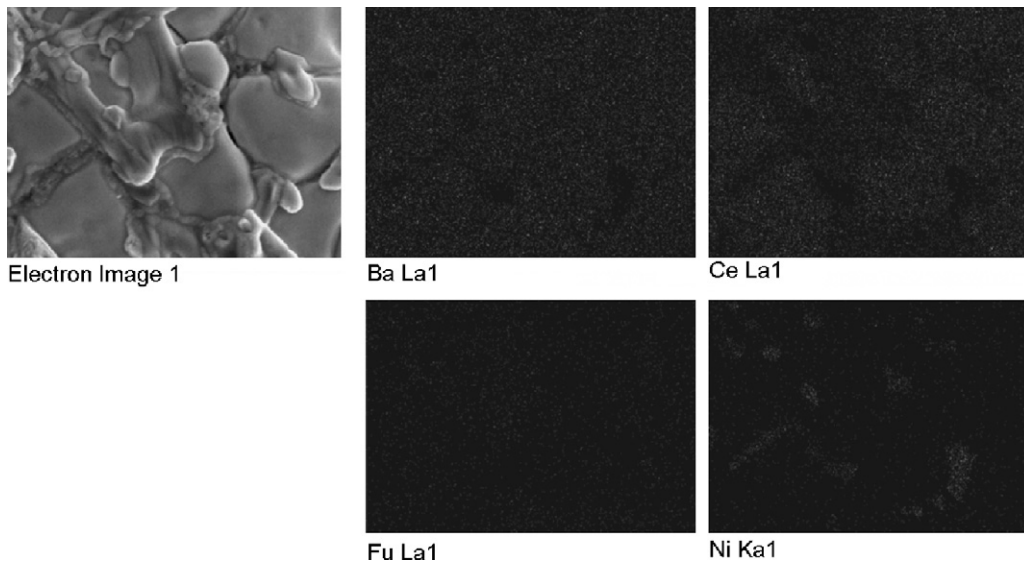

Fig. 10. EDS elemental mapping of sintered (1400 °C) NiO–BCE anode surface.
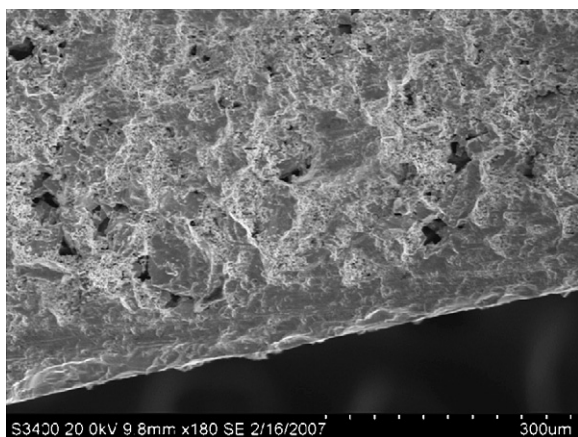
Fig. 11. Cross-section SEM micrograph of NiO–BCE supported BCGP co-sintered at 1400 °C.

in turn would allow the cell performance to increase. Fig. 8 shows an SEM micrograph for a BCGP electrolyte coated on a NiO–BCE anode. The electrolyte/anode structure was sintered at 1400 °C. The large grains seen in the micrograph indicate that the electrolyte is very dense. No secondary phases were detected in the micrograph. Fig. 9 shows an SEM micrograph of NiO–BCE anode surface sintered at 1400 °C; both SE and backscattered modes are shown. The micrographs show that the NiO wet the BCE grains but did not react with the BCE. This microstructure is desired since reaction between the various anode components results in decreased fuel cell performance. Fig. 10 shows EDS element maps for the anode shown in Fig. 9. The maps clearly show that the constituent elements of BCE are contained within the BCE grains and that Ni is only detected in the NiO regions. These data confirm that no reaction compounds were formed.

Fig. 11 is an SEM micrograph showing the cross-section of a NiO–BCE/BCGP anode/electrolyte structure. The layers were co-sintered at 1400 °C. The NiO–BCE anode layer appears in the upper half of the micrograph and the BCGP electrolyte layer is the thin strip appearing in the lower half of the micrograph. The figure shows that the BCGP electrolyte layer adhered well to the NiO–BCE anode. The thickness of the electrolyte was uniform and the electrolyte was very dense. No interfacial reaction layers are seen in the micrograph. These data suggest that an anode supported fuel cell incorporating a NiO–BCE anode and a BCGP electrolyte is viable. Future work will concentrate

on fabricating an anode supported fuel cell based on this anode and electrolyte. In addition, alternative cathode materials will also be investigated in order to replace the relatively expensive Pt cathode with less expensive materials.

4. Conclusions

High performance single element intermediate temperature direct ammonia fuel cells using doubly doped barium cerate electrolyte and a mixed ionic and electronic conducting cermet anode have been successfully demonstrated. The catalytic activity of the Ni–BCE cermet anode towards ammonia was superior to that of a Pt anode. The data suggest that fuel cells incorporating this anode can be operated at temperatures as low as 450 °C, albeit with some loss in performance. The fuel cell was stable for extended periods of time, in excess of 500 h. Future work will be directed at producing an anode supported fuel cell using this novel cermet anode. Alternative cathode materials will also be investigated.

Acknowledgments

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