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A direct ascorbate fuel cell with an anion exchange membrane

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HIGHLIGHTS

- This is first report of an alkaline ascorbate fuel cell.
- The ascorbate fuel cell is more efficient in alkaline than acid.
- Ascorbate has similar efficiency to smaller polyalcohols.

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ABSTRACT

Ascorbic Acid (Vitamin C) is investigated as a renewable alternative fuel for alkaline direct liquid fuel cells (DLFCs). The environmentally- and biologically-friendly compound, L-ascorbic acid (AA) has been modeled and studied experimentally under acidic fuel cell conditions. In this work, we demonstrate that ascorbic acid is a more efficient fuel in alkaline media than in acidic media. An operating direct ascorbate fuel cell is constructed with the combination of L-ascorbic acid and KOH as the anode fuel, air or oxygen as the oxidant, a polymer anion exchange membrane, metal or carbon black anode materials and metal cathode catalyst. Operation of the fuel cell at 60 °C using 1 M AA and 1 M KOH as the anode fuel and electrolyte, respectively, and oxygen gas at the cathode, produces a maximum power density of 73 mW cm^{-2}, maximum current density of 497 mA cm^{-2} and an open circuit voltage of 0.90 V. This performance is significantly greater than that of an ascorbic acid fuel cell with a cation exchange membrane, and it is competitive with alkaline DLFCs fueled by alcohols.

1. Introduction

1.1. *The ascorbic acid fuel cell*

Previous studies demonstrated that ascorbic acid is a strong candidate for use as an alternative fuel for direct liquid fuel cells (DLFCs). For instance, Fujiwara et al., demonstrated that a maximum power density of 15 mW cm^{-2} could be attained with the use of a carbon (rather than precious metal) anode catalyst at room temperature. Their study primarily focused on the current density provided by the anode, which is the limiting reaction in many DLFCs and heavily dependent on double-layer capacitance when carbon is used [1,2]. Moreover, similar work was performed by Uhm et al., by pore-filling the electrolyte into the microstructure of the carbon electrode to increase polar functionality on the surface of the electrode. This proposed modified carbon electrode was favorable in producing a power density of 18 mW cm^{-2} at 60 °C [3]. A separate study conducted by Y. Zeng et al., concentrated on mathematical modeling and investigation of the direct ascorbic acid fuel cell (DAAFC) with an emphasis on the kinetics and mass transfer between the layers of solution and catalyst. When L-ascorbic acid was applied to the model, it was concluded that the limiting factors of the overall fuel cell performance were the concentration of ascorbic acid and the cathode reaction. A higher concentration of ascorbic acid should result in larger power densities, along with variations to anode/cathode capacitance, catalysts, and operating temperature [4].

Mondal et al. showed cyclic voltammagrams utilizing polyaniline (PANI), an inexpensive conducting polymer, on stainless steel (SS) electrode in 0.5 M H_2SO_4 and 0.1 M ascorbic acid (AA). An oxidation peak was observed between a potential range of 0.3 and 0.4 V vs SCE. It was observed that the peak current increased as AA concentration increased and as sweep rate increased. There was also a peak potential shift as sweep rate increased. Furthermore, no

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cathodic peak appeared in the cyclic voltammagrams. These observations indicated AA oxidation was irreversible on a PANI/SS electrode [5]. Furthermore, Mondal et al., performed fuel performance studies on various loadings of PANI. They observed an increase in current density as voltage decreased from the open-circuit potential of 0.5V. Also, an increase in fuel cell temperature resulted in a decrease of open circuit voltage. However, fuel cell performance increased as temperature increased from 27 °C to 70 °C which suggested that an operating DAAFC is viable at a wide range of temperatures. A maximum power density of 4.3 mW cm^{-2} was observed at 70 °C with a current density of 15 mA cm^{-2}. This indicated further that an operating DAAFC can be achieved on an inexpensive anodic catalyst [5].

Karim-Nehzad et al., performed electrochemical studies of ascorbic acid on a glassy carbon electrode modified with cobalt hydroxide in alkaline solution. They observed an increase in oxidation rate and peak current intensity at low potentials, which is thermodynamically more favorable. The modified electrode showed promising electrocatalytic activity for the oxidation of ascorbic acid at 0.565 V vs. SCE combined with 0.1 M NaOH electrolyte solution [6]. Senthil Kumar et al., demonstrated the electrochemical oxidation of AA on a glassy carbon electrode modified with poly 3,4-ethylenedioxythiophene (PEDOT)-modified. A sharp peak oxidation of AA occurred at about −0.035 V on the modified electrode resulting in a cathodic shift from 0.25 V on the bare glassy carbon electrode. These findings may be due to electrostatic interactions between the surface groups on the PEDOT film electrode and the negatively charged ascorbate analyte upon oxidation [7].

1.2. *Ascorbic acid fuel*

Ascorbic acid is an inexpensive compound that is environmentally and biologically friendly. It is a stable and non-toxic powder that is soluble in water yet can also be stored in air [2,4,8]. AA is obtained from the fermentation or chemical conversion of D-glucose, so it is classified as a biomass-derived fuel and could be utilized in a wide range of applications as a regenerative fuel [4,5,8]. In vivo, L-ascorbic acid is oxidized to the nontoxic product dehydroascorbic acid (DHAA), suggesting that AA could be used as a fuel in implantable devices [1,2,4,8,9]. The proton conductivity of AA makes it possible to be used in portable or miniaturized fuel cells using fabrication approaches such as combination of thin film materials with micro-electro-mechanical system (MEMS). For example, Wu et al., demonstrated an operating miniature silicon wafer fuel cell utilizing L-ascorbic acid as a fuel and containing a thin polymer electrolyte as a separator between the reactants, L-ascorbic acid and air. A thin Pt layer was directly deposited on a silicon surface by sputtering and was used as the anodic catalyst for L-ascorbic acid electro-oxidation [10]. Mogi et al., reported fabrication of miniaturized DAAFC with microchannels fabricated on polyimide (PI) substrates. Aluminum electrodes were formed on the PI substrate by photolithography and screen printing. Screen printing was used to deposit porous carbon on the Al electrode surface to increase surface area. These devices are examples of the wide variety of micropower sources that could be utilized for telemetry sensing systems in vivo, demonstrating great flexibility and durability [11]. Furthermore, Falk et al., notably fabricated a microscale membrane-less biofuel cell contact lens for glucose-sensing. The cell utilized ascorbate as the fuel and oxygen as the oxidant present in human lachrymal fluid to generate electricity. Nanostructured microelectrodes were modified with tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) as the anode catalyst for ascorbate oxidation. A redox enzyme, Bilirubin oxidase (BOx), was used as the cathodic catalyst for oxygen reduction. The device remarkably produced a maximum power density of 0.72 μW cm^{-2} with a maximum current density of 0.55 μA cm^{-2}. These results signified that this device could be used as a safe, reliable power source for noninvasive glucose-monitoring [12].

Several studies have demonstrated that the electro-oxidation of AA fuel can be performed on an inexpensive, non-noble metal catalyst unlike fuels such as methanol, ethanol, and polyalcohol fuels that require expensive precious metals for oxidation. Fujiwara et al. demonstrated an operating DAAFC with a cation exchange membrane and a variety of anode catalyst surfaces such as Pt, Ru, Pd, Ir, Rh, PtRu and carbon black (Vulcan XC72) [1,9,13]. Amongst these precious metal catalysts, Pd black exhibited the best performance. However, carbon black anode (12–15 mW cm^{-2}) exhibited maximum power densities two times higher than Pd black metal catalyst (7 mW cm^{-2}). The observed fuel cell performance differences on each anodic catalyst are attributed to the electrochemically active surface area of the electrodes. Furthermore, AA acts as a proton conductor similar to the Nafion ionomer, a proton exchange ionomer that has been used to replace the electrolyte in acid fuel cells. It was shown that increasing mass or thickness of nafion ionomer may inhibit mass transfer of AA toward the electrode surface, thus reducing the rate of oxidation [1,9,13].

1.3. *The alkaline fuel cell*

The alkaline anion exchange membrane (AEM) for the alkaline DLFC has provided advantages over the cation exchange membrane (e.g., Nafion) used in acid DLFCs [14–18]. In alkaline DLFCs, the water is produced at the anode so that water management is minimal, and the cathode does not limit the overall fuel cell performance. Alkaline fuel cells require less activation overpotential, exhibit faster reaction kinetics, and provide a less toxic and less corrosive environment for the fuel cell components, especially the metal catalysts. Finally, the liquid fuels used efficiently in the alkaline DLFC can be handled, stored, and transported more easily than hydrogen [17–23]. Direct ethanol fuel cells (DEFC) garnered the most interest with the first viable AEM several years ago [14,16,18,22,24–29]. Since then many more fuels have been studied in alkaline DLFCs that oxidized very inefficiently in acid DLFCs. Renewable fuels such as ethylene glycol, propylene glycol, and glycerol have shown promise in alkaline DLFCs with power densities as high as 117 mW cm^{-2} at elevated temperature [21,29–31]. Despite advances in technology that permit the use of alcohols in alkaline DLFCs, there is still a need to develop a fuel cell using alternative fuels in efforts to improve the overall fuel cell efficiency and reduce the material costs. Hence, the objective of our work is to study the efficiency of L-ascorbic acid as a fuel in an alkaline DLFC.

2. Experimental

The ascorbate fuel cell contained two distinct catalysts, palladium anode catalyst (Sigma Aldrich, 20–40 m^2 g^{-1} specific surface area, 4 mg cm^{-2} total loading) and platinum black cathode catalyst (Alfa Aesar, 20–40 m^2 g^{-1} specific surface area, 2 mg cm^{-2} loading) in order to utilize the most efficient catalysts for ascorbate oxidation and oxygen reduction, respectively. The catalyst inks were prepared by the combination of 400 μL of water (18.2 Ω cm) and alkaline ionomer suspension (Tokuyama, 5 wt% AS-4) that provided an ionomer to catalyst mass ratio of 1:6. Approximately 2 mg cm^{-2} of each metal catalyst was directly spray painted on an active 4 cm^2 area of an A201 alkaline anion exchange membrane (Tokuyama). At the anode, an additional 2 mg cm^{-2} of Pd was hand-painted to form the anode gas diffusion electrode, however an unmodified carbon cloth was used for cathode gas diffusion layer [32]. A serpentine flow channel was used to supply the fuel at the anode and either