

A Proton Exchange Membrane Fuel Cell with a Pt-Free Cathode and a Freely Diffusing Electron Acceptor

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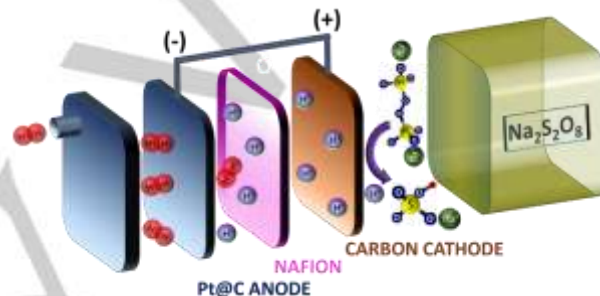
Abstract: In a fuel cell almost 80% efficiency loss arises due to the cathode, consequently the cathode requires the largest amount of precious metal catalyst. Here we show a precious-metal-free cathode for a proton exchange membrane fuel cell (PEMFC) containing only carbon nanoparticles as catalyst and a freely diffusing molecule as electron acceptor. Factors controlling the true rate of electrochemical reactions are amplified just with carbon nanoparticles leading to a carbon corrosion free PEMFC delivering 154 mW/cm² at 358 mA/cm² without any precious metals.

having highly positive standard reduction potential (2.08 V) as the electron acceptor.^[20] The anodic configuration is analogous to that of a conventional PEMFC wherein H₂ is used as the anodic fuel with a Pt supported on carbon (Pt@C) electrocatalyst. The half-cell reactions are provided in equations 1 and 2 and the theoretical voltage expected based on these reactions is 2.08 V.

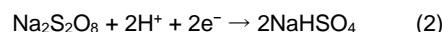
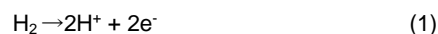
1. Introduction

Shifting to hydrogen economy is perceived as an ideal solution to reduce carbon footprint and associated environmental issues.^[1-3] Impressive research activities have been directed in this direction to mass produce H₂ by splitting water either electrochemically or photo-electrochemically.^[4-6] This is because the chemical energy stored in the chemical bonds of fuel molecules can be later converted into electricity by means of a proton exchange membrane fuel cell (PEMFC).^[7-9] PEMFC can facilitate the distribution of renewable energy to location and times where it is not available. However, the state of the art PEMFC technology is hindered by the inevitability of expensive precious metal catalysts, such as Pt, Pd and Ru, both on the anode and cathode sides to accelerate the reactions to a level required for practical applications.^[10-13] Nevertheless, the cathode side always limits the overall performance of a PEMFC because of sluggish oxygen reduction reaction (ORR) kinetics and therefore demands higher catalyst loading to achieve the required performance level.^[14,15] Extensive research have been put in this direction to replace Pt on the cathode side by non-precious electrocatalysts, yet Pt reigns as supreme cathode electrocatalyst in a PEMFC.^[16-19]

Here we report a new PEMFC configuration (Scheme1) wherein the cathode compartment consists of only carbon nanoparticles as electrocatalyst with a freely diffusing Na₂S₂O₈



Scheme 1. Schematic representation of H₂/Na₂S₂O₈ fuel cell.



2. Results and Discussion

Figure 1a shows the linear sweep voltammogram of a glassy carbon electrode in aqueous Na₂S₂O₈ solution, demonstrating the absence of any faradaic reactions. However, on coating the GC electrode with Ketjen black carbon nanoparticles (KB@GC) there is a clear reduction wave and the reduction current demonstrated an increasing trend with increase in the concentration of Na₂S₂O₈, Figure 1b. Plots of peak current vs. square root of scan rate ($v^{1/2}$) demonstrated a linear behavior and the log (i) vs. log (v) plot furnished a slope of 0.5 for the persulphate reduction on KB@GC electrode demonstrating a diffusion controlled process, Figure S1 (see Supporting Information). Long term stability tests assessed at a potential corresponding to mixed kinetics (0.8 V vs. SHE) region, suggest that KB@GC maintains higher currents for a longer time compared to bare GC electrode, Figure 1c. Exchange current density normalized to the true electrochemically active area (S_{act}) on KB@GC is found to be 4.16×10^{-6} A/cm² which is ~5.7 times higher than that on bare GC (7.32×10^{-7} A/cm²) electrode demonstrating an electrocatalytic effect of carbon nanoparticles towards persulphate reduction (Figure 1d). S_{act} of electrodes was estimated based on the cyclic voltammogram obtained for a freely

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