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A Vitamin C Fuel Cell with a Non-bonded Cathodic Interface

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Vitamin C is a naturally occurring molecule with antioxidant properties often playing pivotal role in many chemical and biochemical processes. We show that a cobalt based molecular electrocatalyst can mediate the electron donation from vitamin C that on coupling with a non-bonded and reversible electron acceptor, the electron flow between the half cells can be channeled in a precious metal free configuration. The non-bonded nature of the electron acceptor allowed fast interfacial kinetics even on simple carbon particles and arrested the cathode derived parasitic chemistry often encountered with molecular oxygen, the conventional electron acceptor in fuel cells. Consequently, the vitamin C fuel cell driven by non-bonded cathodic interface demonstrated performance metrics ~18 times higher than precious metal based vitamin C-O₂ configuration. The renewable nature of the fuel and the precious metal free configuration in proposed non-bonded architecture noticeably reduce the cost of electricity per kW with potential practical applications for powering commercial electrical-appliances.

1. Introduction

Electrochemical energy storage and conversion devices have great potential to address climate change and adverse effects of anthropogenic pollution.¹⁻⁹ Fuel cells have received significant attention in this regard as they are potential zero emission energy conversion devices.⁶⁻⁹ Small molecule based fuel cells like direct alcohol fuel cells, direct borohydride fuel cells, direct hydrazine fuel cells etc., are projected by the safety and storage issues associated with hydrogen fuel.¹⁰⁻¹⁷ Vitamin C is another potential small molecule to be used fuel cells because of its abundance in natural resources and low reduction potential.¹⁸⁻²⁴ Vitamin C is often used in many synthetic strategies as reducing agents owing to its low reduction potential.²⁵⁻²⁹ It belongs to the category of essential nutrients with antioxidant properties and is a medication for many diseases such as scurvy, drug poisoning, liver disease, atherosclerosis, schizophrenia etc.³⁰⁻³² Here we show a vitamin C fuel cell where its catalysis is mediated by a cobalt based molecular electrocatalyst leading to a Pt free anodic half-cell chemistry. To

design a Pt free fuel cell, the conventional electron acceptor O₂, is replaced by an outer sphere or a non-bonded redox species which can undergo facile electron transfer even on carbon based electrodes.³³⁻³⁶ The vitamin C fuel cell driven by non-bonded cathodic interface delivered performance metrics ~18 times higher than precious metal based vitamin C-O₂ fuel cells due to fast anode as well as cathode interfacial kinetics and the absence of parasitic chemistry involving the cathodic interface. Interestingly, the catholyte in proposed configuration is electrochemically reversible, leading to a hybrid fuel cell redox flow battery system. We further demonstrate the use of precious metal free vitamin C fuel cell to power commercial electrical appliances suggesting feasibility for practical applications.

2. Results and Discussion

2.1. Anodic Half Cell Chemistry

The precious metal free vitamin C fuel cell is shown in scheme 1, constituting an anodic half-cell with a cobalt based phthalocyanine (CoPc) molecule as the anodic electrocatalyst for vitamin C oxidation and a cathodic half-cell containing an outer sphere electron acceptor (Potassium ferricyanide) that can undergo fast and reversible redox chemistry on carbon based electrodes. The anodic and cathodic cells were separated by a cation conducting Nafion 117 membrane to prevent internal short circuit. The mediation of vitamin C oxidation by cobalt based molecular electrocatalyst is visible in the cyclic voltammogram, Figure 1a wherein the addition of Vitamin C made the reduction peak of Co³⁺ to disappear (inset of Figure 1a) and fuel oxidation commenced at the position of Co²⁺ to Co³⁺ oxidation, suggesting an EC_{cat} mechanism.³⁷⁻³⁹ The onset and peak potentials are significantly shifted negatively when compared to a Pt based and carbon based electrodes, clearly demonstrating an electrocatalytic effect of CoPc towards vitamin C oxidation, Figure 1b and Table S1, supporting information. Investigation of long term stability by

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