



Performance comparison of protonic and sodium phosphomolybdo vanadate polyoxoanion catholytes within a chemically regenerative redox cathode polymer electrolyte fuel cell



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HIGHLIGHTS

- Four polyoxometalate catholytes are investigated in a regenerative fuel cell.
- The catholytes vary in terms of vanadium content, counter ions and pH.
- Thermodynamic properties, cell performance and regeneration rates are reported.
- Steady state system performance generates insights into formulation optimization.

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ABSTRACT

The direct reduction of oxygen in conventional polymer electrolyte fuel cells (PEFCs) is seen by many researchers as a key challenge in PEFC development. Chemically regenerative redox cathode (CRRC) polymer electrolyte fuel cells offer an alternative approach via the indirect reduction of oxygen, improving durability and reducing cost. These systems substitute gaseous oxygen for a liquid catalyst that is reduced at the cathode then oxidised in a regeneration vessel via air bubbling. A key component of a CRRC system is the liquid catalyst or catholyte. To date, phosphomolybdo vanadium polyoxometalates with empirical formula $H_{3+n}PV_nMo_{12-n}O_{40}$ have shown the most promise for CRRC PEFC systems. In this work, four catholyte formulations are studied and compared against each other. The catholytes vary in vanadium content, pH and counter ion, with empirical formulas $H_6PV_3Mo_9O_{40}$, $H_7PV_4Mo_8O_{40}$, $Na_3H_3PV_3Mo_9O_{40}$ and $Na_4H_3PV_4Mo_8O_{40}$. Thermodynamic properties, cell performance and regeneration rates are measured, generating new insights into how formulation chemistry affects the components of a CRRC system. The results include the best CRRC PEFC performance reported to date, with noticeable advantages over conventional PEFCs. The optimum catholyte formulation is then determined via steady state tests, the results of which will guide further optimization of the catholyte formulation.

1. Introduction

Issues surrounding cost and durability continue to inhibit the widespread commercialisation of polymer electrolyte fuel cells (PEFCs) across both stationary power and automotive sectors [1,2]. The main cause of these problems is the direct 4-electron reduction of oxygen at the cathode. Due to relatively slow kinetics [3,4], conventional PEFCs require high platinum loadings to catalyse the oxygen reduction reaction (ORR), increasing the cost of the membrane electrode assembly (MEA) [5]. Even with increased amounts of catalyst, the oxygen reduction reaction can be the source of more than half the voltage loss in a PEFC system [6]. The presence of air at the cathode is also a key

component in the major mechanisms of fuel cell degradation, including high voltage transients at cell start-up and shut-down [7,8] and chemical degradation of membranes via highly oxidative species [9,10].

Fig. 1 illustrates the alternative approach of chemically regenerative redox cathode (CRRC) PEFCs, which utilise the indirect reduction of oxygen [11]. The anode is essentially identical to that of a conventional PEFC, with hydrogen gas supplied via a flow field through a gas diffusion layer onto a catalyst (platinum) coated membrane. The difference lies on the cathodic side of the cell, where a liquid catalyst (catholyte) circulates between the cathode and an air-liquid contacting reactor called the “Regenerator”. At the cathode, the electrochemical reduction of the catholyte is relatively facile and can be conducted at

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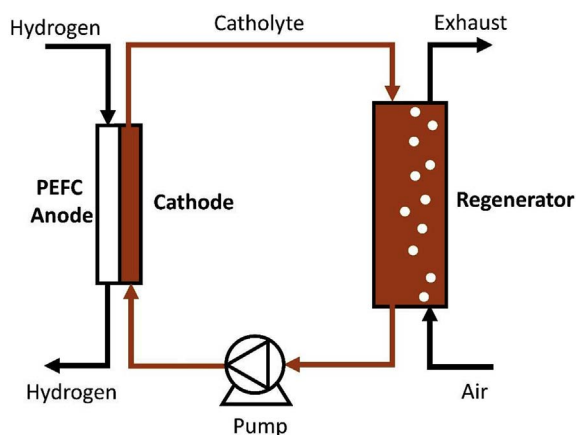


Fig. 1. Schematic diagram of a CRRC PEFC system.

carbon rather than platinum, significantly reducing the cost of the MEA. Subsequent catholyte re-oxidation, via air bubble infusion, is conducted within the regenerator, where oxygen is reduced to water. The result is a fuel cell where gaseous air never enters the cathode, eliminating the major PEFC degradation mechanisms. In addition, the catholyte ensures the membrane remains well hydrated, negating the requirement for gas humidification and allowing operational temperatures greater than 80 °C.

Posner first proposed the CRRC concept in 1955, using a bromine/bromide redox couple for the catholyte [12]. In the early 1980s, the Ford Motor Company were one of the first to employ a vanadium(IV)/vanadium(V) couple in a CRRC catholyte, although they struggled to replicate the performance of conventional PEFCs [13,14]. Since then, several researchers and organisations have further developed the concept using a range of catholyte redox chemistries including $\text{Fe}^{2+}/\text{Fe}^{3+}$, HNO_3/NO and polyoxometalates (POMs) [11,15–21]. A notable contribution was from ACAL Energy Ltd, who operated a CRRC PEFC for over 10,000 h on an automotive test cycle with negligible loss in cell performance and almost commercialised their system [22]. The most advanced CRRC PEFC system reported to date used a POM-vanadium (IV)/vanadium(V) catholyte and disclosed headline performance figures of 0.90 V at 0.2 A cm⁻², 0.72 V at 1 A cm⁻² and a maximum power of 1.00 W cm⁻² [21]. This is comparable with that of conventional fuel cells [23], suggesting the platinum-free technology could be close to market deployment.

A key component of the CRRC PEFC system is the catholyte. An effective catholyte must possess several properties: a relatively high redox potential to ensure high thermodynamic efficiency; good ionic conductivity and facile electrode kinetics to allow for acceptable cell performance; and fast regeneration kinetics to maintain a reasonable operating voltage [11]. To date, the most developed CRRC catholytes are aqueous solutions of polyoxometalates (POMs) incorporating kegginn-type mixed-addenda heteropolyanions of general formula $\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}^{(3+n)-}$, denoted HPA-*n* [24]. The α -kegginn structure is shown in Fig. 2 and consists of a central tetrahedral PO_4 ion surrounded by twelve MO_6 distorted octahedra, where M is the metal (in this case either Mo or V). For a fully oxidised HPA-*n*, the Mo and V addendum atoms are in oxidation states 6 and 5, respectively, and the counter cations are often protons or a mixture of protons and Group 1 metal ions [25]. CRRC PEFC systems with such POM-based catholytes utilise the vanadium(V)→(IV) electrochemical reduction and the vanadium (IV)→(V) chemical oxidation. Although these catholytes often have the empirical formula of a kegginn molecule, for *n* > 1 they exist as an equilibrium mixture of keggins, free vanadium, free phosphate and other ionic species [26–29]. For example, a fully oxidised aqueous solution of empirical formula $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ contains VO_2^+ , phosphate and the keggins $[\text{PV}_4\text{Mo}_8\text{O}_{40}]^{7-}$, $[\text{PV}_3\text{Mo}_9\text{O}_{40}]^{6-}$, $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ and

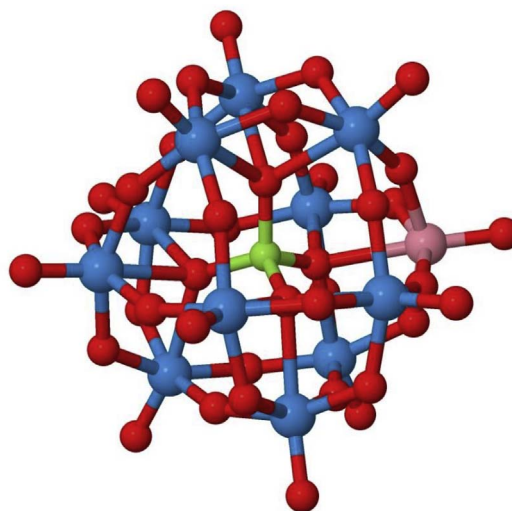
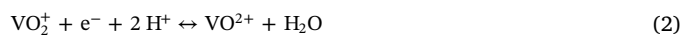
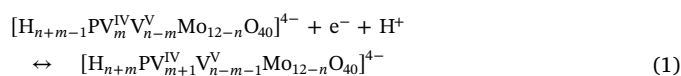
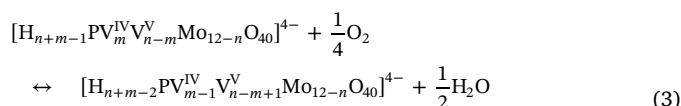


Fig. 2. Representation of the α -kegginn structure $[\text{PV}_1\text{Mo}_{11}\text{O}_{40}]^{4-}$ with phosphorous in green, molybdenum in blue, vanadium in pink and oxygen in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$[\text{PV}_1\text{Mo}_{11}\text{O}_{40}]^{4-}$ [21]. The speciation depends on the total POM concentration, pH, temperature and additional cations present in solution [26–28]. Reduced solutions of $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ also contain vanadium (IV) species, present as VO^{2+} and/or reduced keggins. Consequently, the cathode reduction reaction involves the reduction of vanadium(V) to (IV) in both free and kegginn bound forms, where $1 \leq n \leq 4$ and $0 \leq m \leq 4$ [30]:



In contrast, the catholyte oxidation reaction occurring in the regenerator only involves reduced keggins [31,32]. The reaction is thought to follow a 3 or 4-electron pathway involving an intermediate activated complex [33], but for simplicity can be written as:



Despite the importance of the catholyte formulation, the literature on POM-formulation effects in CRRC PEFCs is sparse. The only substantial study of formulation was conducted by Matsui et al., who investigated $\text{H}_3\text{P}\text{Mo}_{12}\text{O}_{40}$, $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ at different temperatures and concentrations [19]. They also varied pH in dilute solutions (0.01 M) of $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ and found pH played a key role in system performance. Although the researchers found 0.3 M $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ at 80 °C gave the optimum system performance, their best peak power density was ~ 40 mW cm⁻², much lower than that of conventional fuel cells. Recently, Gunn et al. reported a high performance CRRC PEFC using 0.3 M $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ as the catholyte, achieving a peak power density of 1000 mW cm⁻² [21]. In addition, the researchers established several key measurement techniques to assess the catholyte over a range of reduction levels, with focus on catholyte redox potential, regeneration rate, cell power density and steady state system performance. In the present study, the same methodology and high-performance system is used to investigate the effect of three key parameters on the catholyte, namely vanadium content, pH and sodium content. First, a catholyte with empirical formula $\text{H}_6\text{PV}_3\text{Mo}_9\text{O}_{40}$ (HV3) is compared with $\text{H}_7\text{PV}_4\text{Mo}_8\text{O}_{40}$ (HV4), both catholytes having concentration 0.3 M. HV4 is expected to demonstrate

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