

A highly selective platinum-free oxygen cathode for the Swiss-roll mixed-reactant direct borohydride fuel cell

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The performance, durability and cost of the various PEM fuel cell stack components (membrane, electrodes, bipolar flow-field plates) in conjunction with the complex thermal and water management, are some of the major challenges hampering the larger scale adoption of fuel cell technology. In 2012, Aziznia et al.^{1,2} introduced an innovative Swiss-roll architecture for mixed-reactant fuel cells both in monopolar and bipolar mode that addresses many of the above-mentioned challenges of fuel cell technology by eliminating the need for ion exchange membranes and bipolar flow-field plates, while providing a lighter, more compact, cylindrical stack architecture. In the Swiss-roll mixed-reactant fuel cell (SR-MRFC) design, a flexible sandwich of electrodes and separators is rolled around an electronically conductive central axis to give a compact 3D electrode space for the fuel cell reactions. The fuel and oxidant is mixed and fed to the reactor as a single stream.

As shown previously^{1,2}, manganese oxide-based electrocatalysts are attractive cathodes because of their abundance, low cost and high electrocatalytic activity toward the ORR. However, the ORR activity of manganese oxide-based electrocatalysts is adversely affected in the presence of borohydride ions, decreasing the OCV and fuel cell performance³. The electrocatalytic selectivity is paramount for the operation of any mixed-reactant system and also for many direct PEM fuel cells (because of fuel crossover to the cathode). Therefore, development of a more selective and active platinum-free ORR electrocatalysts is important to the commercialization of SR-MRFC, and is the focus of the present study.

Among the platinum-free ORR electrocatalysts under research and development, the transition metal, nitrogen and carbon group, commonly abbreviated in literature as M-N-C, are attractive candidates due to their high surface area, high activity, and low cost. Such electrocatalysts can be prepared by high temperature treatment of either macrocyclic compounds or a combination of transition metal precursor and a source of carbon-nitrogen.

The previous generations of M-N-C catalysts prepared in UNM group were optimized for use in conventional fuel cell systems^{4,5}. Such conventional electrodes require high surface area material with pore sizes of 30-60 nm for best accessibility of active sites by oxygen and effective water removal. To be used into the SR-MRFC, the catalyst had to be re-designed to keep the ability of supplying oxygen to the active sites and, at the same time, to be resistant to flooding by the NaBH₄+NaOH mixture. In the present work, the UNM team has modified the synthesis method by decreasing surface area of silica support and decreasing precursor-to-

silica ratio to meet the requirement for application in a SR-MRFC.

Figure 1A shows the electrochemical characterization of the synthesized Fe-AAPyr catalyst in the ORR. The catalyst is very active with $E_{1/2} \sim 930$ mV vs. RHE, which is higher than that of commercial Pt/C catalysts (not shown). Figure 1B represents the tolerance of Fe-AAPyr in NaBH₄ electrooxidation, making this selective electrocatalyst suitable for mixed-oxygen direct borohydride systems. The anodic overpotential for BH₄⁻ oxidation on the Fe-AAPyr electrocatalyst is higher than 0.5 V vs. RHE, which shows promising selectivity for the ORR.

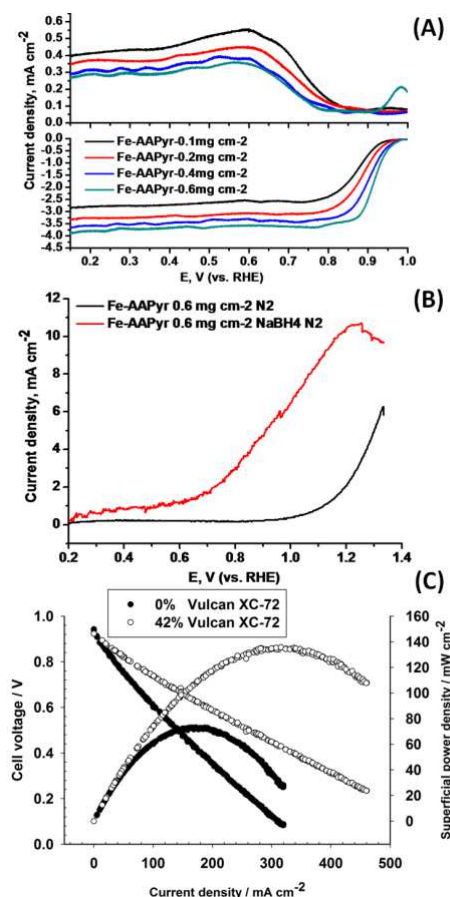


Fig.1 (A) RRDE of Fe-AAPyr with various loadings on working electrode in 1M KOH saturated with O₂ (B) CV of Fe-AAPyr activity toward BH₄⁻ oxidation in 2M NaOH with/without presence of 0.5M NaBH₄ (C) Performance of Fe-AAPyr cathode and effect of Vulcan XC-72 content in a SR-MRFC. Feed: 0.5 NaBH₄, 2 M NaOH+ O₂ 10 SLPM. T=323 K, P= 103 kPa (abs). Separator: Vildeon[®], anode: Pt/C (0.8 mg/cm²) cathode: FeAAyr (loading 6 mg/cm²) GDE

Figure 1C shows the performance of the SR-MRFC with a Pt-FeAAPyr set of electrodes. The OCV was up to 0.97 V, the highest OCV reported for any mixed-reactant system in the literature. The peak power density of 137 mW cm⁻² at 323 K is achieved, which is among the highest power densities reported for the low temperature (T<373 K) mixed-reactant and/or conventional dual chamber PEM DBFCs under similar conditions.

References

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