Operando XAS electrochemical studies of PtNi-Nanowires for the Oxygen Reduction Reaction (ORR) in alkaline electrolyte

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Abstract

Fuel cells (FC) represent an alternative to sustaining the demands of energy for the automobile industry. However, the oxygen reduction reaction (ORR), a significative chemical reaction in FCs occurs poorly in commercial electrolytes, acidic environments. Alkaline electrolyte has proven to promote the ORR for better catalytic responses and accessible commercialization. The use of inexpensive catalysts is suggested for ORR to help its commercialization. In this study we evaluated the performance of PtNi-Nanowires as ORR electrocatalyst. Preliminary results demonstrated current densities of ~ 5 mA/cm^2 with an $E_{1/2}$ = 0.85 V for the PtNi-NWs at 1,600 rpm and 0.012 (mg$_{Pt}$/cm^2) in alkaline medium at (25.00 ± 0.01) °C. Additionally, the number of electrons was calculated using the Koutecký-Levich analysis with temperature-controlled instrumentation resulting n=3.99 ± 0.05. Moreover, durability experiments demonstrated that the PtNi-NWs maintained optimal catalytic activity for ORR along 10,000 cycles. The initial reported $E_{1/2}$ was of 0.817 V and after 10,000 cycles $E_{1/2}$ = 0.812 V, this represents a 5mV change in the $E_{1/2}$. Operando X-ray spectroscopy (XAS) electrochemical experiments were completed to evaluate changes in electronic structure for Ni and Pt. Results showed that the white line of Pt L_3 edge in the PtNi-NWs changed while the electrochemical potential was lowered to negatives values. Showing changes in the electronic structure of Pt. The results presented here suggest that PtNi-NWs is a stable and active catalyst for the ORR in alkaline medium.

Background

The oxygen reduction reaction can proceed via two different chemical reactions in alkaline electrolyte:

- 2 e⁻ pathway:

$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$

- 4 e⁻ pathway:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

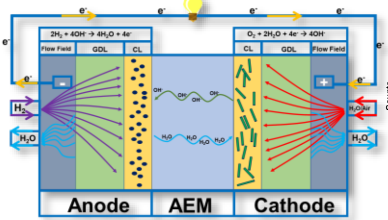


Fig 1: Representation of a hydrogen-based AEMFC with the main species being generated in the cell.

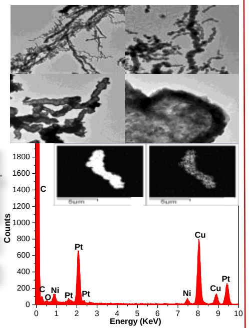


Fig 2: TEM images and EDS mapping of PtNi-NWs.

Electrochemical measurements

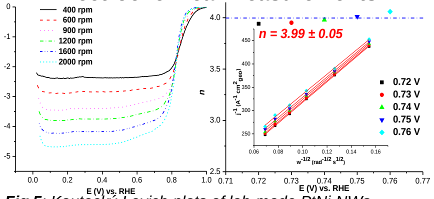


Fig 5: Koutecký-Levich plots of lab-made PtNi-NWs.

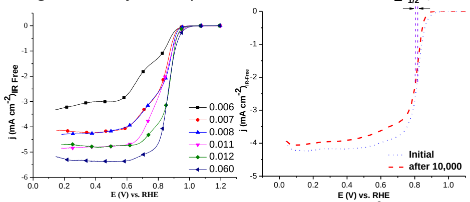


Fig 6: Different mass loadings (mg$_{Pt}$/cm^2) oxygen polarization curves and durability experiments of PtNi-NWs.

Crystal and surface characterizations

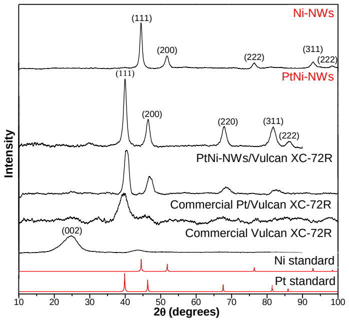


Fig 3: XRD patterns for Ni-NWs and PtNi-NWs.

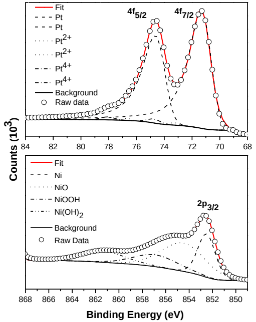


Fig 4: XPS for PtNi-NWs.

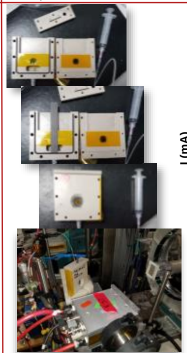


Fig 7: Operando setup.

XAS Results

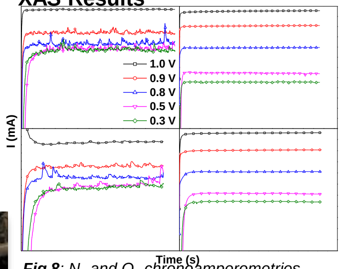
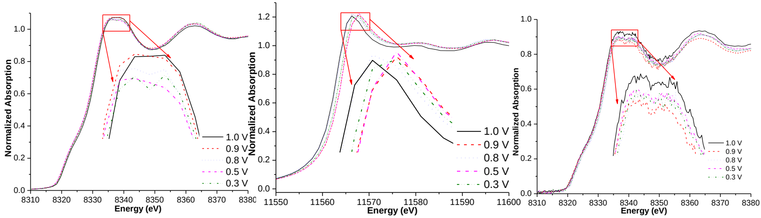


Fig 8: N_2 and O_2 chronoamperometries of PtNi-NWs. 1st row plots while Ni edge and 2nd row while Pt edge. 1st column with N_2 purge and 2nd column with air purge.

XAS Results



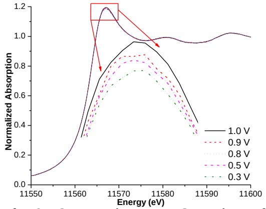


Fig 9: Operando XANES region of Pt-L_3 edge and Ni-K edge with different electrochemical potentials applied to the PtNi-NWs.

Table 1: Structural parameters derived from fitting Ni K edge and Pt L_3 edge.

Sample	Edge	Near Neighbor species	N	R (Å)	σ (Å^2)	E_0 (eV)
Pt foil	Pt L_3	Pt	12	2.764 ± 0.003	0.0055 ± 0.0002	8.0 ± 0.5
Ni foil	Ni K	Ni	12	2.485 ± 0.002	0.0057 ± 0.0002	6.9 ± 0.3
Pt 1.0 V_Air	Pt L_3	Ni	12	2.66 ± 0.03	0.006 ± 0.003	7.8 ± 0.3
		Pt	8.05	2.74 ± 0.03	0.0054 ± 0.0003	
Pt 0.9 V_Air	Pt L_3	Ni	12	2.66 ± 0.03	0.005 ± 0.003	7.7 ± 0.7
		Pt	8.15	2.74 ± 0.03	0.0054 ± 0.0003	
Pt 0.8 V_Air	Pt L_3	Ni	12	2.65 ± 0.03	0.003 ± 0.003	7.5 ± 0.4
		Pt	8.5	2.75 ± 0.03	0.0054 ± 0.0003	
Pt 0.5 V_Air	Pt L_3	Ni	12	2.66 ± 0.03	0.005 ± 0.003	7.4 ± 0.4
		Pt	8.35	2.74 ± 0.03	0.0055 ± 0.0003	
Pt 0.3 V_Air	Pt L_3	Ni	12	2.66 ± 0.03	0.006 ± 0.004	7.0 ± 0.4
		Pt	8.2	2.75 ± 0.03	0.0054 ± 0.0003	

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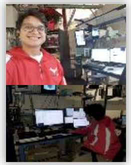

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