Development of Ultra-Low Loading Pt Alloy Cathode Catalyst for PEM Fuel Cells

Branko N. Popov, Tianyuan Xie, Taekeun Kim, Won-Suk Jung, Joseph C. Rotchford, Akos Kriston and Prabhu Ganesan

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208

Hansung Kim

Yonsei University, South Korea

The main strategies to decrease the platinum loading of cathode electrodes are based on optimization of the electrode structures and implementation of more active Pt alloy catalyst and supports. Our strategy to decrease the platinum loading in the cathode is based on (i) synergetic effects of CCC (carbon composite catalyst, free of platinum) on which Pt or Pt alloy catalysts is deposited, thus forming two types of hybrid catalysts Pt/CCC and Ptalloy/CCC (HCC) catalysts [1-5]. The goal of our second strategy is the development of activated graphitic carbon supported Pt alloy catalyst Pt-alloy/AGC (USC) or Ptalloy/CNC -YU. The highly corrosion resistant graphitic carbon is developed at USC and at Yonsei University [5]. The goals are: (i) to achieve kinetic mass activity in H_2/O_2 fuel cell higher than the DOE 2017 target of 0.44 A mg_{PGM}⁻¹, (ii) to demonstrate durability of the kinetic activity per DOE cycling protocol between 0.6 and 1.0 V, and with performance loss less than 40% (iii) to accomplish high current density performance and durability in H_2 /air fuel cell to meet 2017 DOE targets. Cell diagnostics of the cathode catalysts such as ECSA, ORR mass activity, and oxygen polarization curves were performed after 5,000, 10,000, 20,000, and 30,000 cycles. The support durability was studied by applying 1.2 V vs. NHE constant potential with respect to the anode for 400 hours according to the DOE protocol. Cell diagnostics of the cathode catalyst such as ECSA, ORR mass activity, and oxygen polarization curves were performed after 100, 200, 300 and 400 hours.

Pt catalyst was synthesized at USC which shows synergetic effect between the catalytically active nonplatinum CCC support and Pt catalyst. CCC was synthesized with onset potential for oxygen reduction of 0.92 V vs. SHE and with less than 2.5% H₂O₂ production. Our Pt/CCC140 exhibits mass activity of 0.29A/mgPt compared with 0.16 mass activity measured for 46%Pt/C (TKK) catalyst [6]. Mass activity loss after 200 h potential holding was only 24% compared with 58% loss observed for commercial catalyst after 24 hours. The potential holding experiment at 1.2 V for the support durability of Pt/CCC140 showed only 6 mV loss after 200 hours indicating very stable support and catalyst. The observed voltage loss for commercial catalyst was higher than 250 mV after 200 h potential holding test at 1.2 V vs. SHE.

USC hollow graphitic carbon supported Pt catalyst, Pt/AGC after 400 h holding at 1.2 V vs. SHE shows only 33% loss of mass activity compared with 40% loss of 2017 DOE target. The platinum was deposited on inhouse developed support synthesized using three-step procedure. The durability of high current performance of this catalyst under hydrogen air after 400 h potential holding at 1.2 V shows only 3mV loss at 800 mA compared with 30 mV loss of 2017 DOE target.

One dimensional simplified agglomerate-based macro-homogeneous model is developed and was solved analytically and numerically to explain the effect of the parameters that control the mass activity of the catalyst [7-8]. Table 2 summarizes the status of the low Pt alloy catalyst development research.

Table 2 Status of the low-Pt alloy catalyst development research (HCC $_{250}$ and Pt $_2\rm Ni_1/\rm CNC$ catalysts)

	-	
Characteristics	2017 Targets	Status
PGM total	0.125	$0.2 \text{ mg}_{\text{Pt}}/\text{cm}^2$
loading	mg_{Pt}/cm^2	
Mass activity		0.38A/mg _{Pt} <u>HCC₂₅₀</u>
(MA)	0.44A/mg	0.44A/mg _{Pt}
80°C, 100%	@0.9V _{iR-free}	<u>YU Pt₂Ni₁/CNC</u>
RH, 150kPa _{abs.}		
	MA loss ≤40%	USC HCC ₂₅₀
Catalyst		*47% loss (MA)
durability	ECSA loss	*15% loss (ECSA)
30,000 cycles,	≤40%	*53 mV loss (H ₂ -air)
0.6-1.0 V,		
50mV/s,	Current Density	YU Pt ₂ Ni ₁ /CNC
$H_2/N_{2,} 80^{\circ}C,$	$@0.8A/cm^2$ in	*32% loss (MA)
100kPa _{abs} .	H ₂ -air loss	*26% loss (ECSA)
	\leq 30 mV	
	MA loss ≤40%	USC HCC ₂₅₀
Support		*47% loss (MA)
durability	ECSA loss	*42% loss (ECSA)
1.2 V for 400h,	≤40%	*29 mV loss (H ₂ -air)
80° C, H ₂ -N ₂ ,		
150kPa _{abs.,}	Current Density	<u>YU Pt₂Ni₁/CNC</u>
100% RH	$@0.8A/cm^2$ in	*48% loss (MA)
	H ₂ -air loss	*43% loss (ECSA)
	\leq 30 mV	

The current status of the research indicates that the results obtained in the first phase of the project demonstrate promising performance of the mass activity under H_2/O_2 and high current performance under H_2/air and durability of the kinetic mass activity and support stability. In the second phase two catalysts will be selected for further studies.

References

- 1. X. Li, S. Park and B. N. Popov, J Power
- Sources, **195**, 445 (2010). 2. B. N. Popov, X. Li and J. W. Lee, *Int. J. Hyd.*
- *Energy*, **36**, 1794 (2011). 3. S. Y. Huang, P. Ganesan and B. N. Popov, *Appl.*
- *Catal. B: Environmental*, **102**, 71 (2011).
 X. Li, B. N. Popov, T. Kawahara and H. Yanagi, *J. Power Sources*, **196**, 1717 (2011).
- 5. K. H. Lim, H. Oh and H. Kim, *Electrochem. Commun.*, **11**, 1131 (2009).
- 6. P. Mani, R. Srivastava and P. Strasser, J. Phys. Chem. C, 112, 2770 (2008).
- A. Kriston, T. Xie, P. Ganesan and B. N. Popov, J. Electrochem. Soc., 160, F406 (2013).
- A. Kriston, T. Xie, D. Gamliel, P. Ganesan and B. N. Popov, *J. Power Sources*, submitted.

Acknowledgement

The financial support of Department of Energy (DE-EE0000460) is acknowledged gratefully.