Electronic Supplementary Information (ESI)

Shape-tuned surface-active and support-free silver oxygen reduction electrocatalyst enabled high performance fully non-PGM alkaline fuel cell

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Materials: High purity analar grade silver nitrate ($AgNO_3$) and potassium hydroxide (KOH) pellets were purchased from SISCO Research Laboratories Pvt. Ltd., India. High purity analar grade trisodium citrate decahydrate, sodium borohydride, ascorbic acid, ethanol and isopropyl alcohol were procured from Sigma-Aldrich Pvt. Ltd., India. Commercial carbon supported nickel nanoparticles (Ni/C, Premetek, Ni 80%, ~ 30 nm) was used as anode catalyst. Fumion FAA-3-SOLUT-10 ionomer and FAA-3 anion exchange membranes (70 µm thick, 17 $mScm^{-1}$ anion (hydroxide) conductivity at 20 ^{o}C) were from Fumatech. Porous carbon gas diffusion layer (GDL) sheets were purchased from SAI Energy Solutions Pvt. Ltd, India. Hydrogen (99.9%) (H_2), oxygen (99.9%) (O_2) and nitrogen (99.9%) (N_2) were supplied by Indian oxygen limited, India. All glassware was meticulously cleaned using aqua regia and finally rinsed with copious amount of water. Double distilled water (Millipore) was used for all preparative and characterization works.

Silver nitrate (mmol)	**Trisodium citrate decahydrate** (mmol)	**Sodium borohydride** (mmol)	**Ascorbic acid** (mmol)	**Shapes attained**
8	0.75	0.15	0.1	spheres
“	0.375	0.475	0.15	spheres
“	0.6	0.235	0.165	spheres
“	0.3	0.525	0.175	spheres
“	0.5	0.3	0.2	worm-in-sphere
“	0.25	0.4	0.35	worm-in-sphere
“	0.25	0.35	0.4	sphere-in-worm
“	0.125	0.45	0.425	sphere-in-worm
	0.15	0.435	0.415	worms
“	0.1	0.5	0.4	worms
“	0.05	0.5	0.45	worms

Table S1: Details of “hierarchical shape tuning approach” showing the precisely varying ratio of capping agent to dual reducing agents amount and the tuneable shapes obtained from this new approach.

Anode catalyst layer	**Cathode catalyst layer**	**Membrane**	**Non-PGM loading in MEA**	**Cell conditions**	**Power density ($mW\ cm^{-2}$)**	**Power density ($mWmg^{-1}_{non\text{-}PGM}\ cm^{-2}$)**	**Fuel cell stability test**	**Year and reference**
Cr/Ni (5 mg cm^{-2})	Ag (1 mg cm^{-2})	Quaternary ammonium polysulphone	6 mg cm^{-2}	60 °C, H_2/O_2 (RH = 100%)	50	8.3	NA	2008, 48
Ni/C (5 mg cm^{-2})	Ag (0.5 mg cm^{-2})	TPQPOH152	5.5 mg cm^{-2}	70 °C, 200 sccm H_2/O_2	76	13.8	NA	2013, 47
NiW (17.5 mg cm^{-2})	Coppy/C (2 mg cm^{-2})	xQAPS	19.5 mg cm^{-2}	60 °C, 50 sccm H_2/O_2 (RH = 100%)	40	2.05	NA	2013, 49
NiW (17.5 mg cm^{-2})	Coppy/C (2 mg cm^{-2})	xQAPS	19.5 mg cm^{-2}	60 °C, 50 sccm H_2/air (RH = 100%)	27.5	1.4	NA	2013, 49
Ni (1.5 mg cm^{-2})	Ag (3mg cm^{-2})	AAEM	4.5 mg cm^{-2}	73 °C, 200 sccm dry H_2/ 1000 sccm air	70	15.5	NA	2016, 46
Ni/C (1.25 mg cm^{-2})	V-AgNs (0.25 mg cm^{-2})	AAEM	1.5 mg cm^{-2}	60 °C, 500 sccm H_2/ 200 sccm O_2 (RH = 100%)	115.6	75.3	~240 h	Present work
Ni/C (1.25 mg cm^{-2})	S-AgNs (0.25 mg cm^{-2})	AAEM	1.5 mg cm^{-2}	60 °C, 500 sccm H_2/ 200 sccm O_2 (RH = 100%)	41.3	20	~136 h	Present work

Table S2: Fully n-PAAEMFCs performance of the present work comprehensively compared with previous similar literature reports.

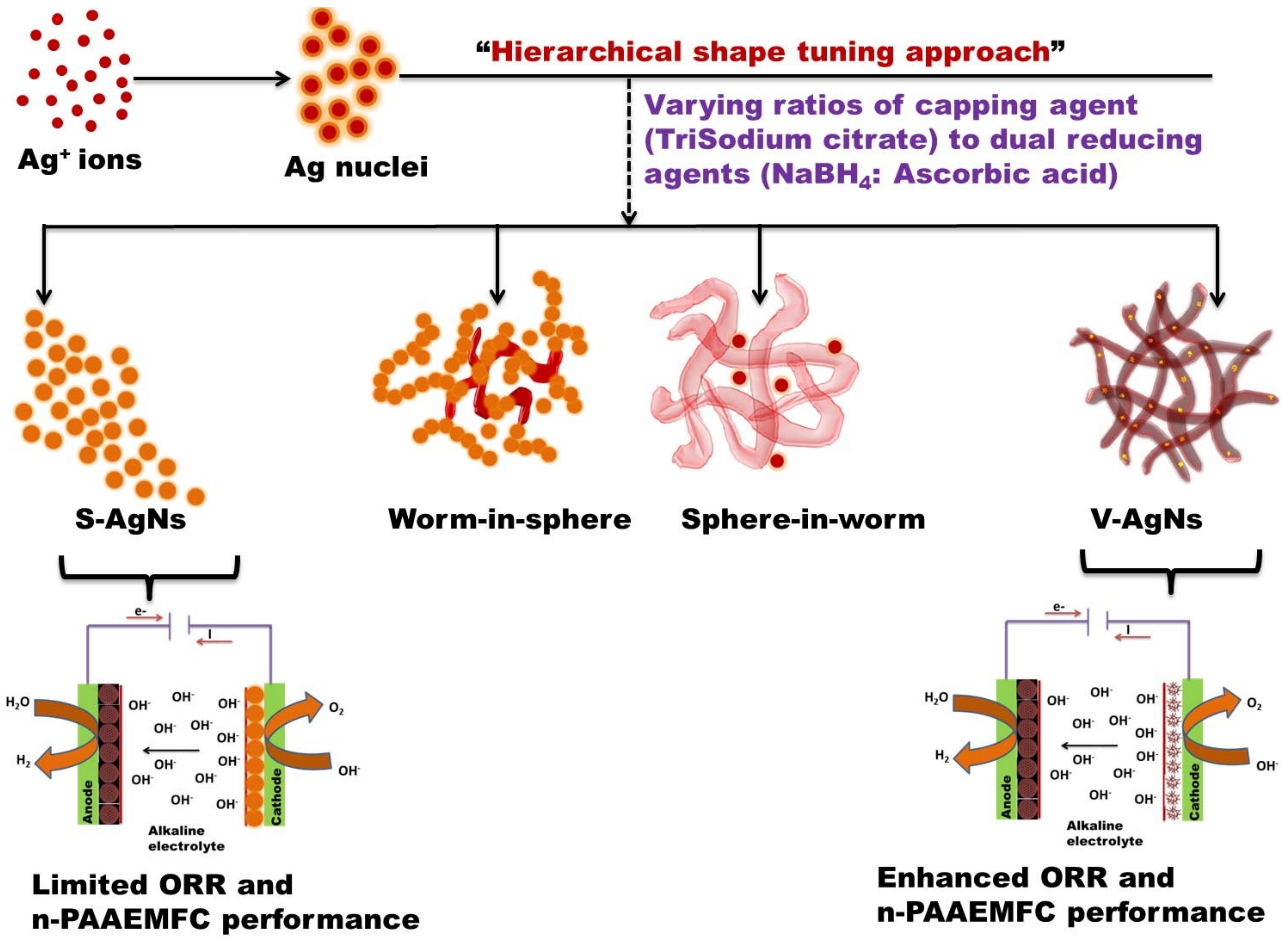

Fig.S1: Table of contents graph showing the hierarchical approach of AgNs synthesis and their application in fully non-PGM alkaline fuel cell.

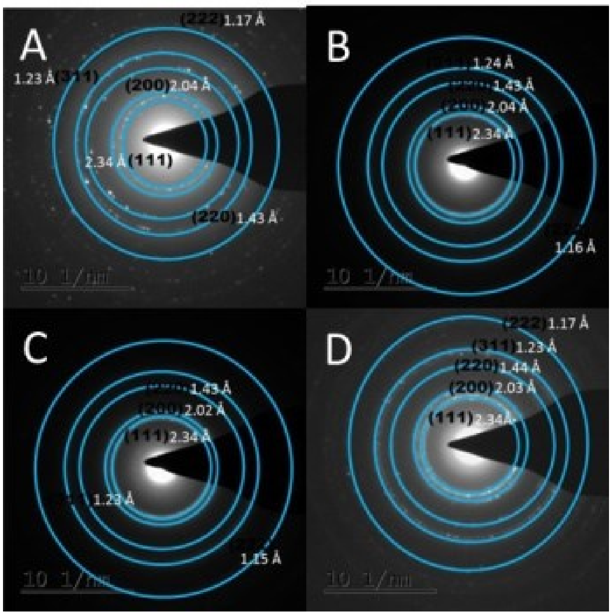

Fig.S2: TEM-SAED patterns of (A) S-AgNs, (B) worm-in-sphere, (C) sphere-in-worm, (D) V-AgNs showing their relevant crystallographic planes and d values.

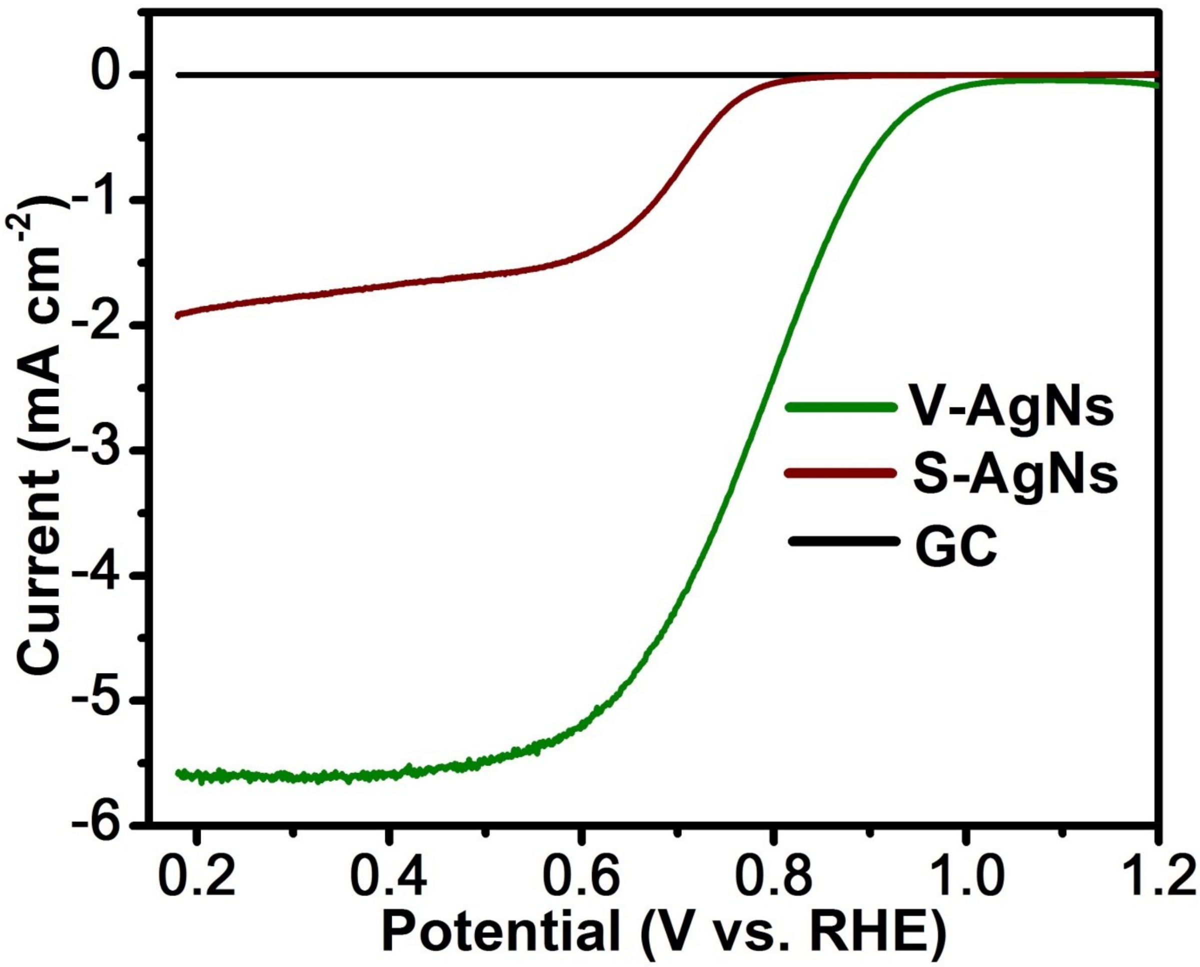

Fig.S3: LSV-ORR performance comparison of GC, S-AgNs and V-AgNs electro-catalysts in O_2 saturated 0.5 M KOH recorded at 5 mV s^{-1}, 1600 rpm.

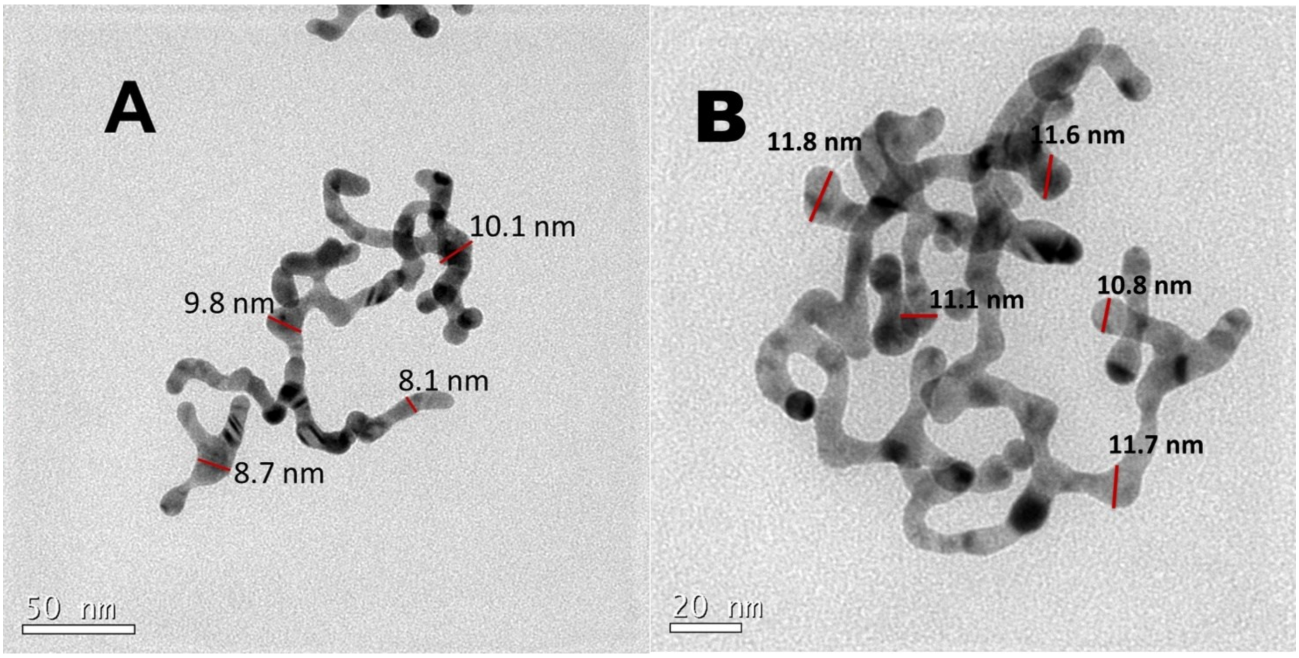

Fig.S4: TEM image of V-AgNs (A) before and (B) after AET studies showing the retention of its unique worm like morphology.

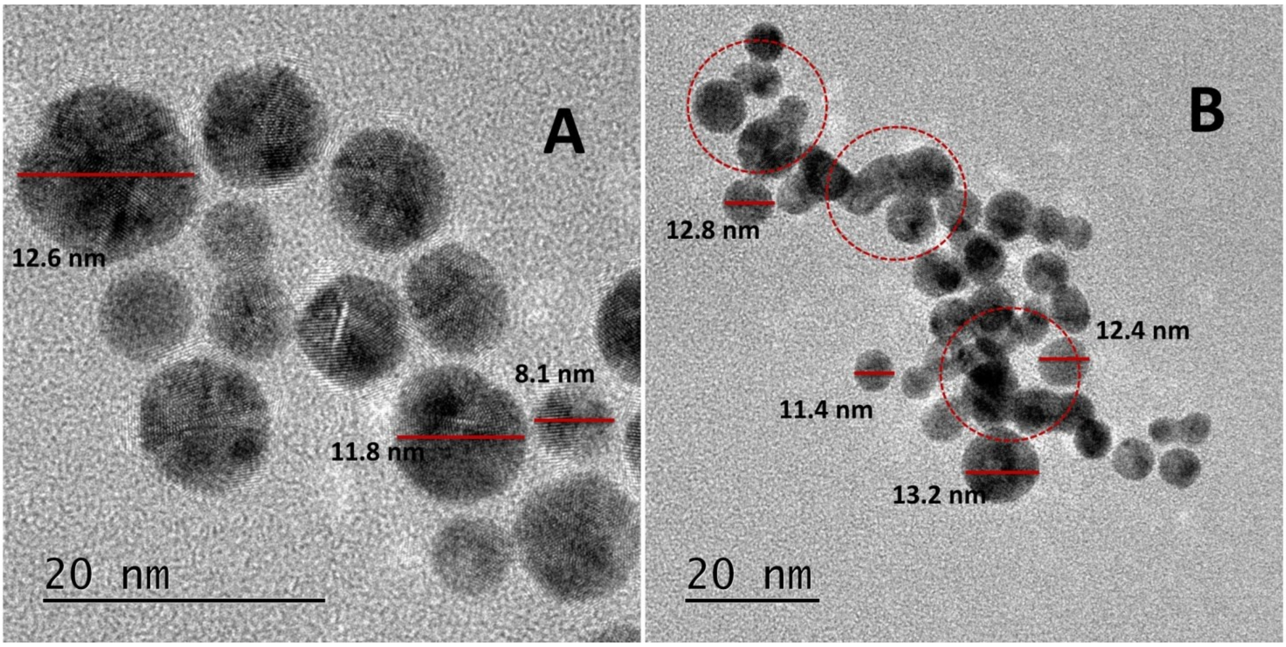

Fig.S5: TEM image of S-AgNs (A) before and (B) after AET studies (Red circles showing the agglomerated Ag nano-spheres after AET).

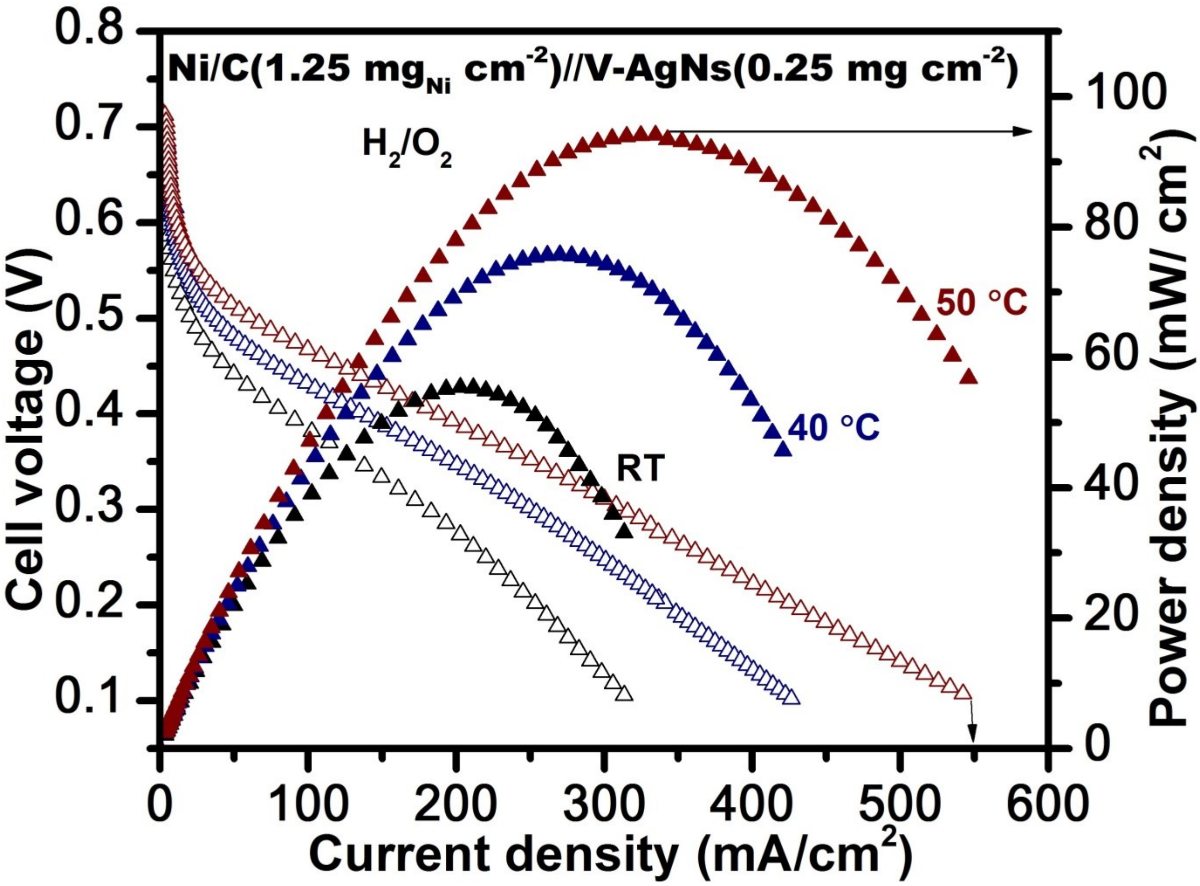

Fig.S6: Fully n-PAAEMFC performance at RT (30 °C), 40 °C and 50 °C between MEAs; anode catalyst layer: commercial NiC, cathode catalyst layer: V-AgNs.

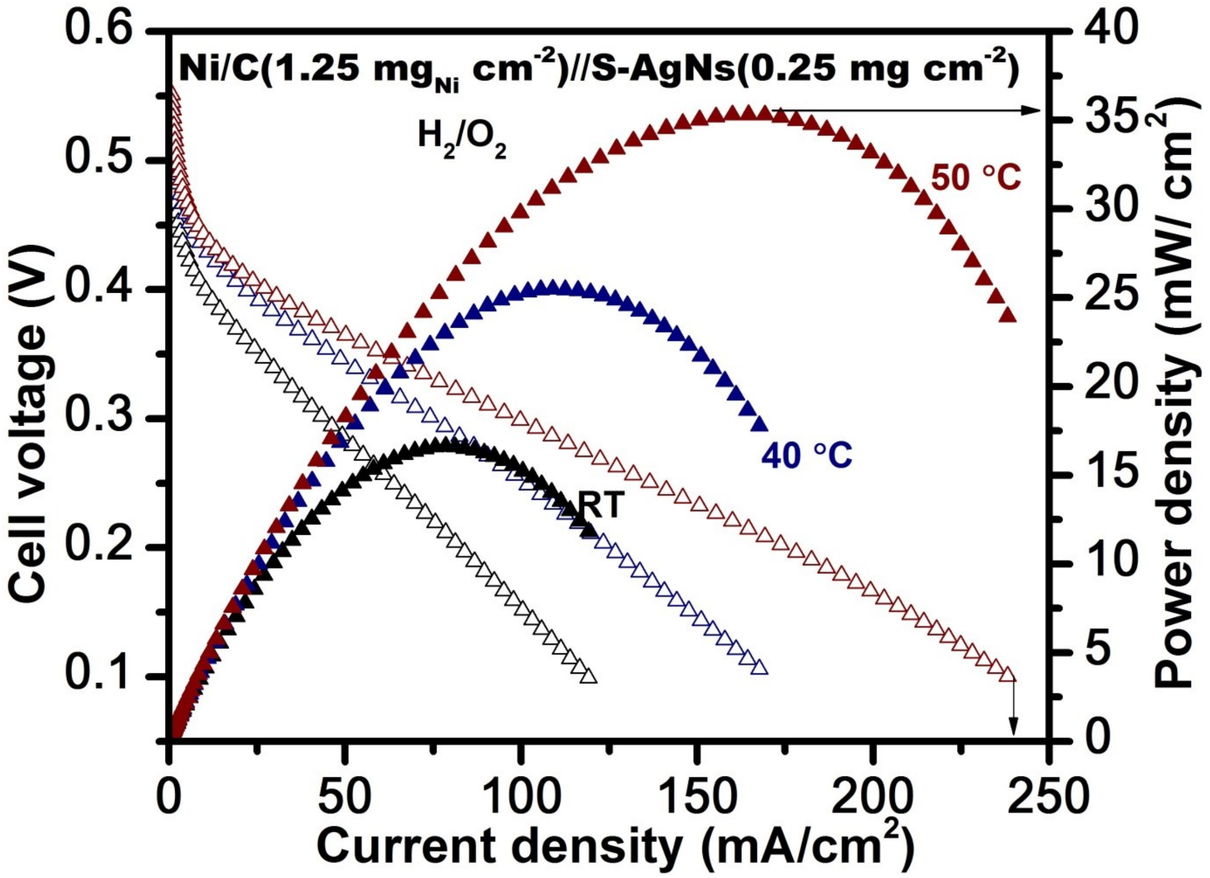

Fig.S7: Fully n-PAAEMFC performance at RT (30 °C), 40 °C and 50 °C between MEAs; anode catalyst layer: commercial NiC, cathode catalyst layer: S-AgNs.