SUPPLEMENTARY MATERIAL

Calculation of the layer thickness on the GC-RDE [34]

For the calculation of the approximate layer thickness on the GC-RDE the quantity (m), the density (ρ) and the volume (V) of metal, Vulcan XC72R and Nafion Ionomer solution, as well as the area of the GC-RDE (A_{GC}) were used. For the different catalysts, the loading (ω) of metal and Vulcan XC72R was also considered.

$$layer\ thickness = \frac{\frac{m_{metal}}{\rho_{metal}} + \frac{m_{Vulcan\ XC72R}}{\rho_{Vulcan\ XC72R}} + \frac{m_{Nafion\ 5\ wt.\%}}{\rho_{Nafion}}}{A_{GC}}$$

$$m_{metal} = \frac{m_{catalyst}}{V_{mixture}} \cdot V_{catalyst\ ink} \cdot \omega_{metal(=\ 0.4\ or\ 0.3\ or\ 0.2\ or\ 0.1)}$$

$$m_{Vulcan\ XC72R} = \frac{m_{catalyst}}{V_{mixture}} \cdot V_{catalyst\ ink} \cdot \omega_{Vulcan\ XC72R\ (=\ 0.6\ or\ 0.7\ or\ 0.8\ or\ 0.9)}$$

$$m_{Nafion\ 5\ wt.\%} = \frac{\rho_{Nafion\ 5\ wt.\%} \cdot V_{Nafion\ 5\ wt.\%} \cdot \frac{5}{100}}{\frac{V_{mixture}}{V_{catalyst\ ink}}}$$

$m_{catalyst} = 8.1\ mg\ for\ all\ PdNiBi/\ C\ \ catalysts$

$V_{Nafion\ 5\ wt.\%} =\ 13\ \mu L\ Nafion\ ionomer\ solution$

$V_{mixture} = 1.75\ mL\ 2 - propanol +\ 0.737\ \mu L\ ultrapure\ water +\ V_{Nafion\ 5\ wt.\%} = 2.5\ mL$

$V_{catalyst\ ink} = 10\ \mu L\ (2\ times\ 5\ \mu L)\ were\ applied\ on\ GC - RDE$

$A_{GC-RDE} = Area\ of\ the\ GC - RDE = 0.196\ cm^2$

$\rho_{metal} = Density\ of\ Pd\ (12.02\ g\ cm^{-3})\ and\ Ni\ (8.91\ g\ cm^{-3})\ and\ Bi\ (9.78\ g\ cm^{-3})$

$\rho_{Nafion} = 1.98\ g\ cm^{-3}$

$\rho_{Nafion\ 5wt.\%} = 0.94\ g\ cm^{-3}$

$\rho_{Vulcan\ XC72R} = 0.096\ g\ cm^{-3}$

Table S1: Results of the layer-thickness calculation on the GC-RDE.

Catalysts	Layer thickness / μm
PdNiBi/C (40/60)	10.5
PdNiBi/C (30/70)	12.2
PdNiBi/C (20/80)	13.9
PdNiBi/C (10/90)	15.6

34. Cermenek, B.; Genorio, B.; Winter, T.; Wolf, S.; Connell, J.G.; Roschger, M.; Letofsky-Papst, I.; Kienzl, N.; Bitschnau, B.; Hacker, V. Alkaline Ethanol Oxidation Reaction on Carbon Supported Ternary PdNiBi Nanocatalyst Using Modified Instant Reduction Synthesis Method. *Electrocatalysis* **2020**, *11*, 203–214. 10.1007/s12678-019-00577-8.

Table S2. Chemical composition of the PdNiBi/C active-catalyst material determined by ICP-MS (Bi) and AAS (Pd, Ni) in at.%.

Catalysts	measured			calculated		
	Pd	Ni	Bi	Pd	Ni	Bi
PdNiBi/C (40/60)	84.0	10.0	6.0	85	10	5
PdNiBi/C (30/70)	84.4	10.2	5.4	85	10	5
PdNiBi/C (20/80)	83.3	10.4	6.3	85	10	5
PdNiBi/C (10/90)	84.6	8.9	6.5	85	10	5

Table S3. XRD data of the $Pd_{85}Ni_{10}Bi_5$/C catalysts.

Peak No.	Crystal structure	Miller indices	Peak Pos. (° 2θ)			
			PdNiBi/C (40/60)	PdNiBi/C (30/70)	PdNiBi/C (20/80)	PdNiBi/C (10/90)
1	Graphite(2H)_187640-ICSD	(002)	25.414	25.447	25.513	25.480
2	Pd_64922-ICSD	(111)	39.505	39.703	39.604	39.736
3	Pd_64922-ICSD	(200)	45.841	46.006	45.940	46.237
4	Pd_64922-ICSD	(220)	67.027	66.796	66.664	66.664

Peak No.	FWHM. (° 2θ)				Crystallite size (nm)			
	PdNiBi/C (40/60)	PdNiBi/C (30/70)	PdNiBi/C (20/80)	PdNiBi/C (10/90)	PdNiBi/C (40/60)	PdNiBi/C (30/70)	PdNiBi/C (20/80)	PdNiBi/C (10/90)
2	1.914	3.300	3.102	3.102	4.6	2.7	2.8	2.8

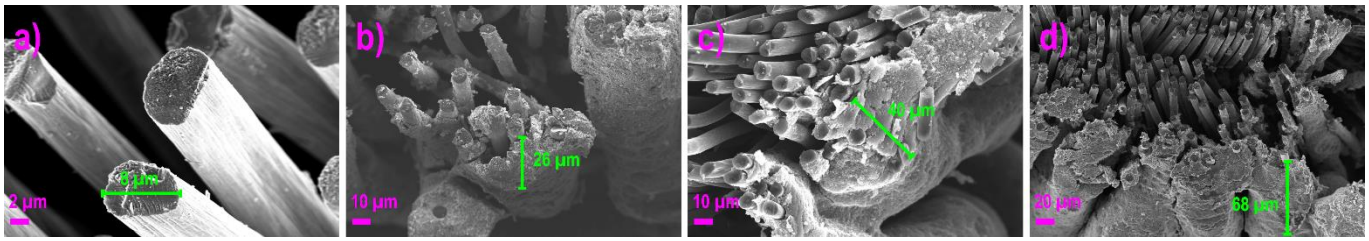

Figure S1. SEM images with the dimensioning of the cross section of the different PdNiBi/C electrodes (catalyst on carbon cloth) (a) without catalyst; (b) with PdNiBi/C (40/60); (c) PdNiBi/C (30/70); and (d) PdNiBi/C (20/80).

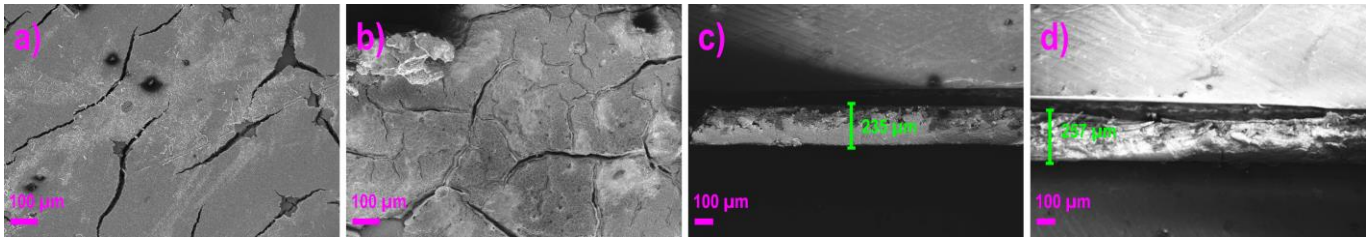

Figure S2. SEM images of the PtRu/C cathode electrodes (a) blank carbon paper; (b) carbon paper with catalyst; (c) cross section of the blank carbon paper; (d) cross section of the carbon paper with catalyst.

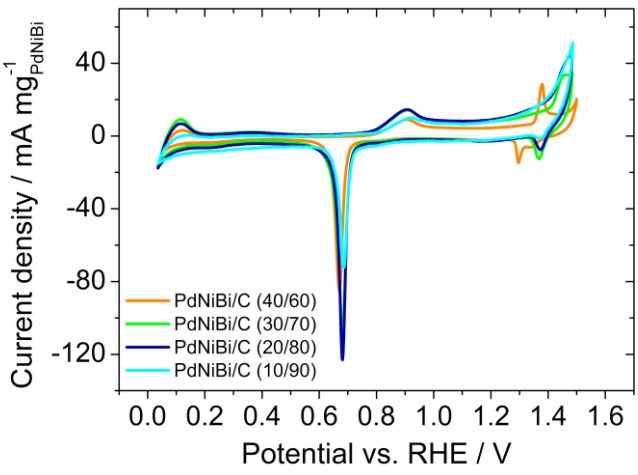

Figure S3. Electrochemical characterization of the PdNiBi/C catalysts with a scan rate of 10 mV s^{-1} at 30 °C in a potential range from 0.05 V – 1.5 V vs. RHE in N_2-purged 1 M KOH.

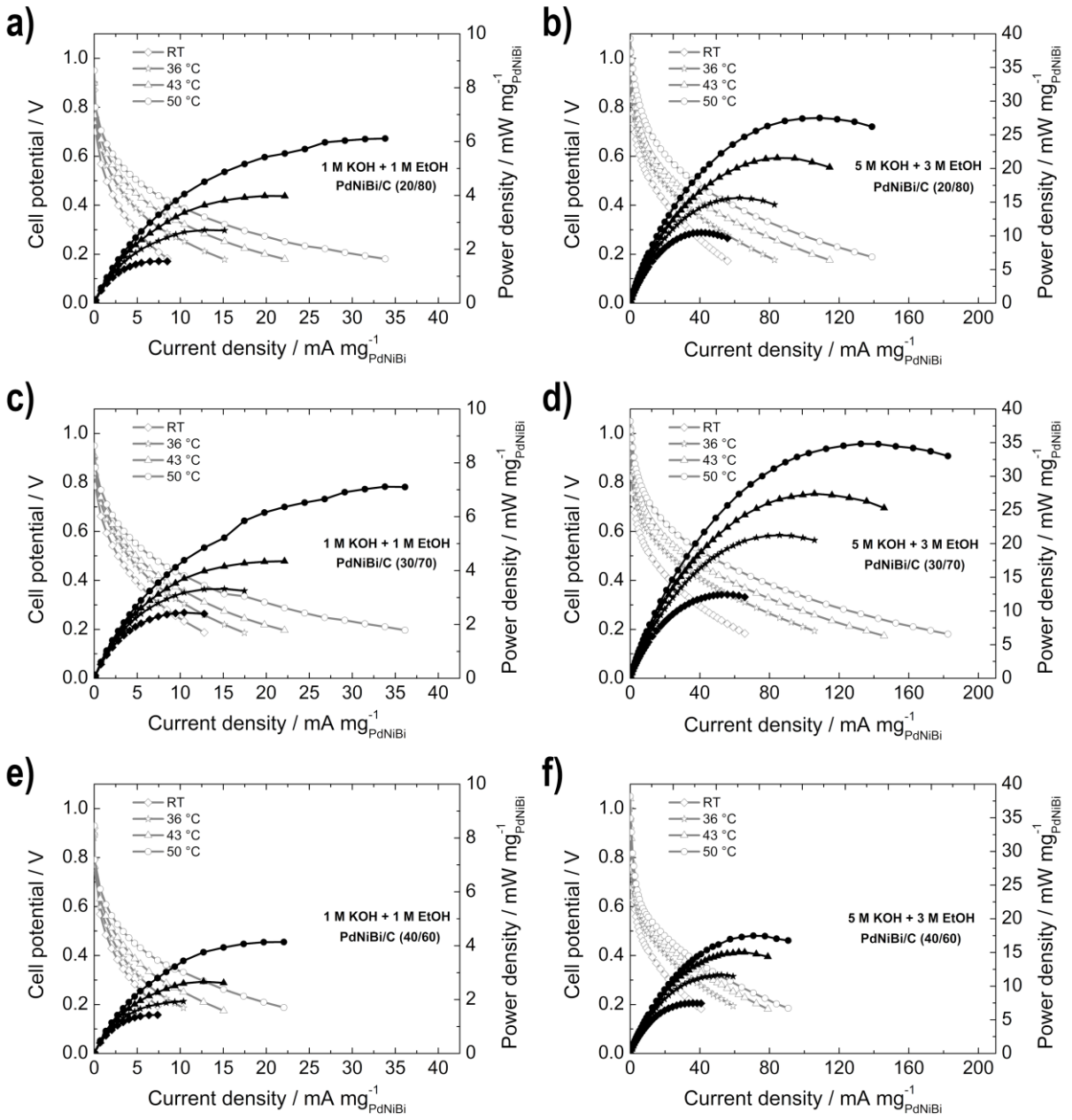

Figure S4. Power density (filled symbols) and polarization curves (unfilled symbols) for the single-cell measurements of the different PdNiBi/C electrodes at different temperatures (RT, 36 °C, 43 °C, 50 °C) and different fuel concentrations (a) PdNiBi/C (20/80), 1 M KOH + 1 M EtOH; (b) PdNiBi/C (20/80), 5 M KOH + 3 M EtOH; (c) PdNiBi/C (30/70), 1 M KOH + 1 M EtOH, (d) PdNiBi/C (30/70), 5 M KOH + 3 M EtOH; (e) PdNiBi/C (40/60), 1 M KOH + 1 M EtOH; and (f) PdNiBi/C (40/60), 5 M KOH + 3 M EtOH.