*Supplementary Material:*

# Active Site Engineering of Intermetallic Nanoparticles by the Vapour-Solid Synthesis: Carbon Black Supported Nickel Tellurides for Hydrogen Evolution

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## Total X-Ray fluorescence spectroscopy

### Recovery rate experiment tellurium

A recovery rate experiment was carried out to assure the accuracy of tellurium concentrations from TXRF investigations. Therefore, 500 µL of a $\beta_{standard}$(Te) = 10 mg $L^{-1}$ tellurium standard solution, 500 µL of a 30 mg $L^{-1}$ gallium standard solution, as internal standard, and 100 µL polyvinyl alcohol solution were mixed. 5 µL of the as-prepared mixture were drop cast onto the sample carrier and dried under IR irradiation for 45 min. After investigation by TXRF the correction factor for tellurium was calculated as $\beta_{standard}$(Te) over $\beta_{TXRF}$(Te). The observed factor was used to correct the tellurium concentrations of all investigated Ni-Te samples.

*Table S 1.: TXRF tellurium recovery rate experiment*

| measurement | $\beta_{TXRF}$(Te) [mg $L^{-1}$] | correction factor |
|---|---|---|
| 1 | 23.07 | 0.43 |
| 2 | 23.87 | 0.42 |
| 3 | 23.87 | 0.42 |
| 4 | 20.36 | 0.49 |
| 5 | 20.22 | 0.49 |

## Sample quantification

*Table S 2.: TXRF sample investigations (Te values are not corrected), 30 mg $L^{-1}$ gallium as internal standard*

| sample | weighed mass [mg] | β(Te) [mg $L^{-1}$] | β(Ni) [mg $L^{-1}$] |
|---|---|---|---|
| Ni/C_16 | 26.51 | - | 42.82 |
| $Ni_{85}Te_{15}$/C | 20.39 | 24.61 | 35.88 |
| $Ni_{78}Te_{22}$/C | 29.10 | 10.12 | 12.08 |
| $Ni_{49}Te_{51}$/C | 16.06 | 46.03 | 12.54 |
| $Ni_{39}Te_{61}$/C | 19.76 | 78.74 | 12.14 |
| Ni/C_7 | 22.86 | - | 16.39 |
| $Ni_{67}Te_{33}$/C | 21.46 | 40.32 | 20.59 |
| $Ni_{85}Te_{15}$/C | 23.39 | 49.56 | 20.14 |

## Powder X-Ray diffraction

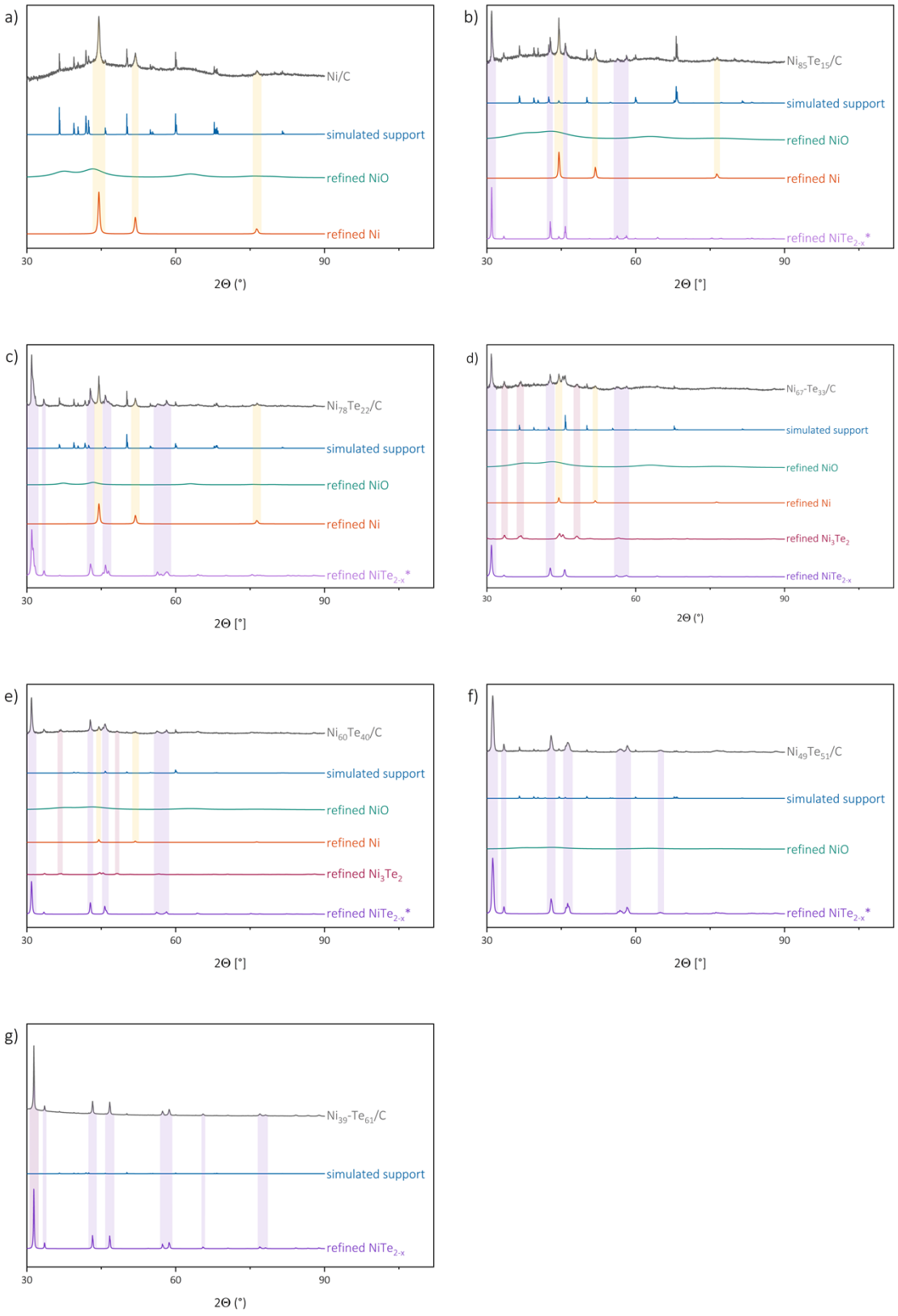


*Figure S 1.: measured and refined tXRF patterns with the most significant peaks highlighted of Ni/C and intermetallic Ni-Te/C samples with ascending Te content from (a) to (g). *combined $NiTe_{2-x}$ patterns with different parameter sets.*

## Physisorption

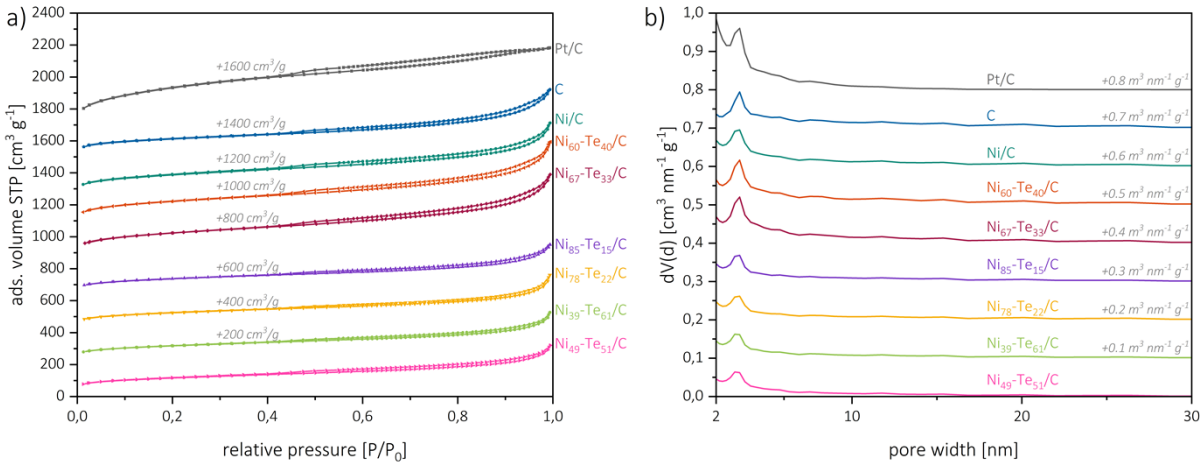


*Figure S 2:Nitrogen physisorption isotherms recorded at -196 °C of carbon black based materials (a) and respective QSDFT pore size distributions (b).*

## Cyclic voltammetry

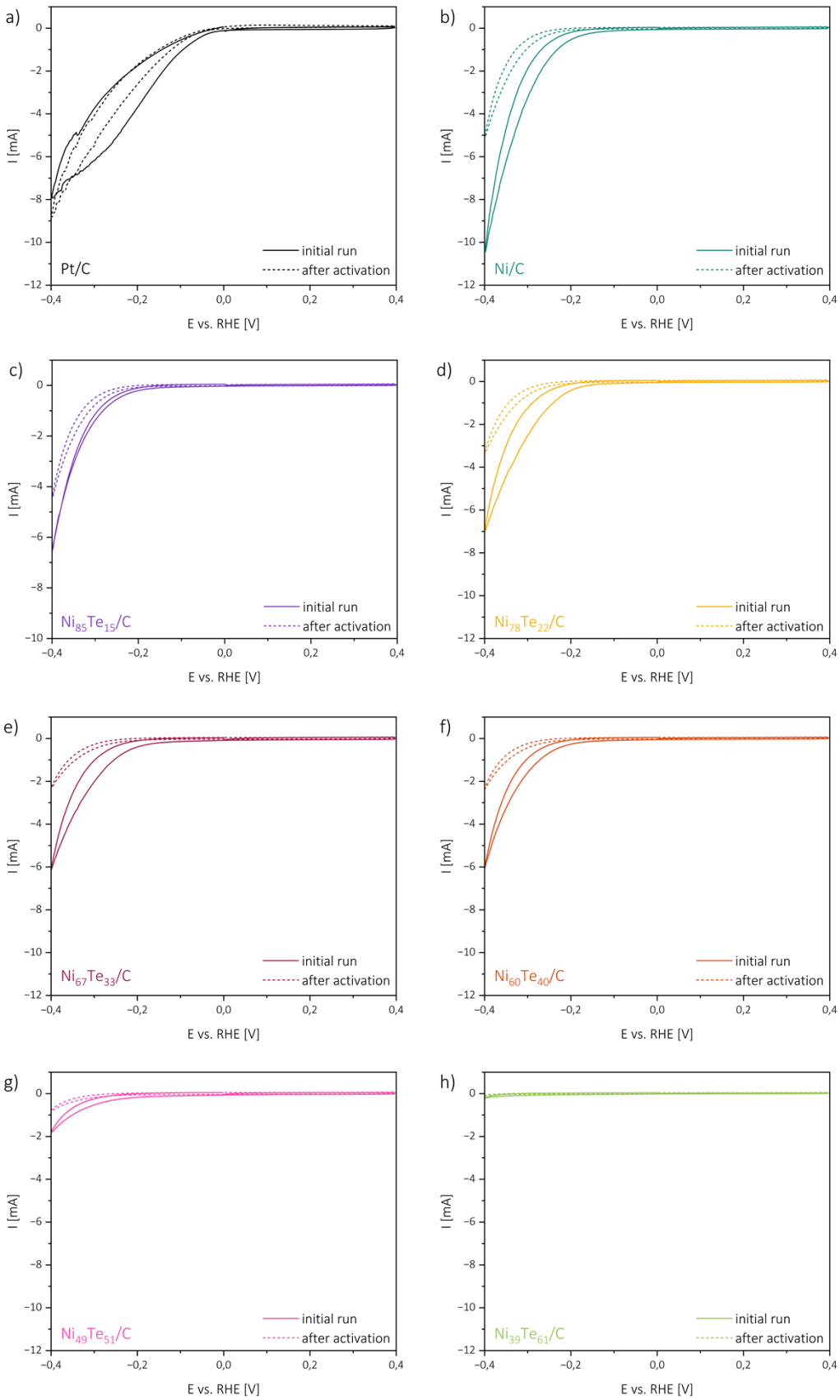


*Figure S 3.: Cyclic voltammetry curves before and after activation from Pt/C (a); Ni/C (b); and intermetallic Ni-Te/C samples with ascending tellurium contents (d) to (h).*

## Double layer capacitance

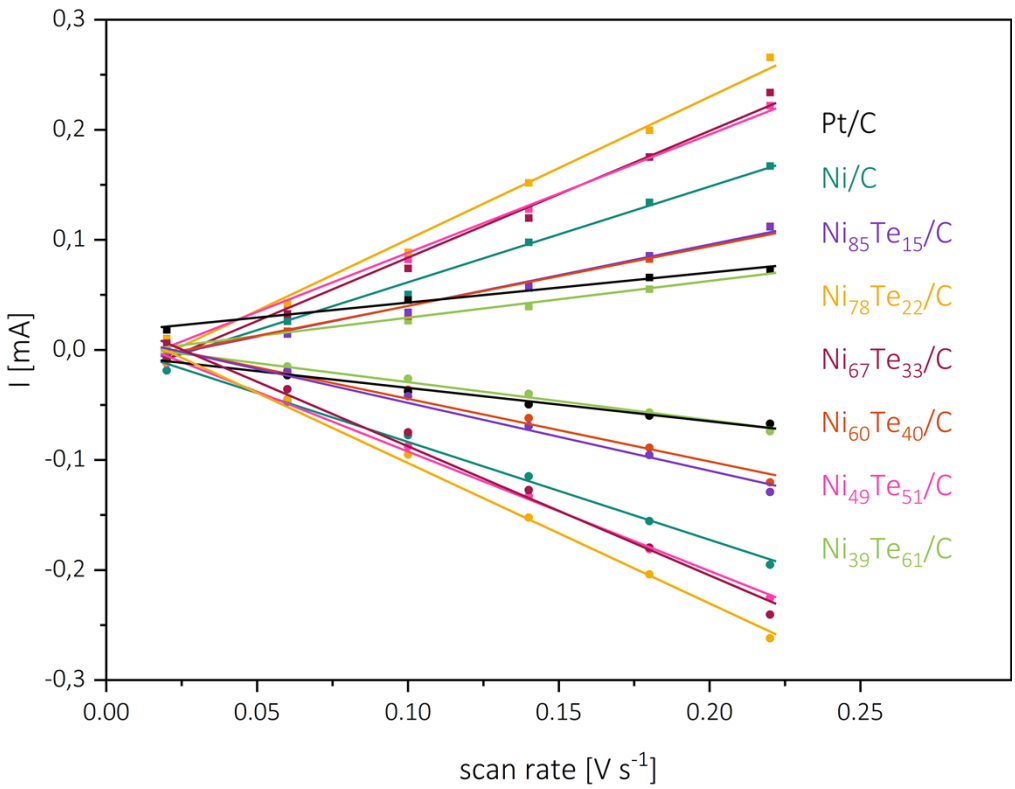


*Figure S 4.: Cathodic (circles) and anodic (squares) charging currents measured at 0.10 V vs. RHE plotted as function of the scan rate. The determined double-layer capacitance of the system is taken as the average of the absolute value of the slope of the linear fits to the data.*

*Table S 3.: Calculated double layer capacitance ($C_{DL}$) of the prepared electrodes.*

| sample | $C_{DL}$ [mF] |
|---|---|
| Pt/C | 0.288 |
| Ni/C | 0.880 |
| $Ni_{85}Te_{15}/C$ | 0.588 |
| $Ni_{78}Te_{22}/C$ | 1.290 |
| $Ni_{67}Te_{33}/C$ | 1.160 |
| $Ni_{60}Te_{40}/C$ | 0.556 |
| $Ni_{49}Te_{51}/C$ | 1.085 |
| $Ni_{39}Te_{61}/C$ | 0.339 |