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Hydrogen evolution in alkaline medium on intratube and surface decorated PtRu catalyst

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ABSTRACT

For anion exchange membrane (AEM) electrolysis, challenges include finding an optimal catalyst for hydrogen evolution reaction (HER), as the noble metals are scarce while non-noble metals are inferior. Here, the noble metal amount is reduced in a straightforward solution synthesis which produces Pt-Ru surface nanoparticles and unique intratube nanowires decorated on single walled carbon nanotubes (SWNT). In half-cell tests, $5 wt_{PtRu}$ -% Pt-Ru SWNT demonstrates stable 10 mA cm⁻² HER current at 46 mV overpotential and outperforms commercial electrocatalysts. When integrated in an AEM electrolyser, a high current density of 500 mA cm⁻² at a low voltage of 1.72 V is achieved with $34 \,\mu g$ cm⁻² metal loading. First-principles calculations reveal that both the Pt-Ru alloy nanoparticle and intratube nanowires promote near optimal H* binding energy, thereby releasing the H₂ faster. Thus, our approach yields an active low metal loading alkaline HER catalyst without sacrificing the performance in an AEM electrolyser.

1. Introduction

An increasing awareness of the environmental and societal impacts of fossil fuels use has increased research efforts to adopt different technologies for harnessing renewable energy [1,2]. Hence, the cost to generate renewable energy is expected to continue decreasing in the future [3,4]. Most of the renewable energy sources are intermittent and therefore, energy storing remains the challenge to balance supply and demand. Today, widely used energy storage technologies include batteries, hydro, fly wheels and compressed air which provide electric power on demand as the output. However, they are either not accessible to all societies (hydro) or can provide only relatively short-term energy storage. Storing renewable energy in chemical compounds, especially hydrogen, in conversion reactions is considered as a potentially viable option for long-term energy storage [5].

Currently, majority of hydrogen (96%) is produced from nonrenewable sources (e.g. coal, natural gas, etc.) releasing CO_2 to the atmosphere [6] and remaining (4%) by electrolysis of water [7]. The latter is a zero-carbon method, less energy intensive with oxygen as a second product. However, the high cost (10.30 US\$/Kg of H_2) and low efficiency (60–80%) limits its widespread use [8]. Hydrogen has high energy density, and its chemically bound energy can be efficiently converted back to electric power in a fuel cell or can be further utilized in industry. The advantage of water electrolysers is the decoupling of power and capacity which means that the energy storage capacity can be increased without increasing the power, unlike for example in batteries [9].

The trend in the field of anion exchange membrane (AEM) electrolysers is to decrease the amount of platinum group metals (PGM) used as a standard catalyst for hydrogen evolution reaction (HER). The reason for this trend is not entirely economical (cost of the catalyst is 8% of overall expenses of electrolyser system), but the limited production rate of PGMs due to their low abundance in the earth's crust [10–12]. Earlier reported methods to decrease the amount of PGMs include decreasing

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the loading of commonly available catalysts while maintaining the high electrocatalytic performance [13–15]. A more drastic approach is the substitution of PGMs with more abundant and less costly materials as HER catalysts [16,17]. Alloys of transition metals have been found as reasonable alternatives due to their high mineral availability and moderate HER activity [18,19]. However, challenges involving low stability and inferior activity in alkaline conditions restrict utilization of transition metals catalysts in an AEM electrolyser [20–22]. While considering low PGM loadings in those devices, the durability is of utmost importance, as with lower catalyst loadings the degradation effects are pronounced [23].

The state of the art cathode catalyst in an AEM electrolyser comprises of high PGM loadings, Pt or Pt/Ru, deposited on carbon black. However, commonly used Vulcan type catalyst support is not stable under alkaline conditions. Single walled carbon nanotubes (SWNT) can be used as an alternative support material as they are more conductive and more stable than conventional Vulcan type support while feasibility of the SWNT support has been recently demonstrated as a low-loading PGM catalysts for HER in acidic media [15,24]. Although above-mentioned studies discuss the development of HER catalysts, especially for an AEM electrolyser, no efforts have been made to demonstrate a stable, low PGMs based SWNT electrocatalyst in alkaline medium.

In this work, a straightforward approach is used to synthesize a new type of Pt-Ru catalyst with low PGM loading on SWNT support. This method has been reported earlier to yield a platinum catalyst distributed entirely on the surface of conductive SWNT support [14] while its durability has been demonstrated for HER in an acidic environment. We modifed this method to obtain unique Pt-Ru intratube nanowires encapsulated within SWNT and spherical surface nanoparticles with a high aspect ratio, which could not be obtained with other methods. This intratube nanowire feature improves the catalyst durability under harsh alkaline conditions. The high HER activity of Pt-Ru SWNT is attributed to the availability of the intratube nanowires to promote the HER while those tend to be inactive for CO adlayer formation in electrochemical surface area (ECSA_{CO}) analysis. Density functional theory (DFT) calculations are used to verify the contributions of both intratube nanowires and surface nanoparticles to the observed HER activity. In general, the Pt-Ru alloys on SWNT facilitates the release of H₂ faster than Pt SWNT or Ru SWNT catalysts, which have higher H* binding energies. Finally, the Pt-Ru SWNT catalyst, selected with the highest activity towards HER, is successfully tested in a two electrode AEM electrolyser device, showing its potential as HER catalyst for this technology.

2. Experimental details

2.1. Chemicals and Materials

TUBALLTM single walled carbon nanotubes (SWNTs) with < 1%impurities were received from OCSiAl. The mean outer diameter of SWNTs is 1.6 \pm 0.5 nm according to the manufacturer. The platinum precursor (H₂PtCl₆ • 6H₂O), Pt/C (20 wt%, HiSPEC® 3000) used for reference catalyst and anode catalyst material (IrOx • 2H2O, Premion®) were purchased from Alfa Aesar. The ruthenium precursor (RuCl₃) and Nafion dispersion (5 wt%) both were obtained from Sigma-Aldrich. PtRu/C (20 wt%, 1:1 at. ratio) as a reference catalyst and carbon cloth (Sigracet 29BC) as a gas diffusion layer (GDL) were obtained from Fuel Cell Store. Fumasep® FAA-3-30 membrane used for membrane electrode assembly (MEA) and Fumion® FAA-3-Film used for ionomer dispersion were bought from Fumatech. Iso-propanol (i-PrOH, 99.6%) and Ethanol (99.5%) were purchased from Fischer scientific and Altia Oy respectively. Solid KOH with 97% purity was received from Sigma-Aldrich. All the chemicals obtained were of analytical-reagent grade and ultrapure ion-exchanged Milli-Q water (Millipore) was used for all water purposes.

2.2. Catalyst synthesis

2.2.1. Step I: Functionalization of SWNTs

The OCSiAl SWNTs were functionalized with an ozone gas fluidized through SWCNTs using an ozone generator (Enaly OZX-300ST). The ozone gas is generated through corona discharge (ozone tube) ozone production technology. A built-in air pump pumps the ambient air via air dryer to feed the ozone tube. An ozone flow of 200 mg/h at the outlet of the ozone generator was utilized to functionalize SWNTs. The pristine SWNTs were weighed in a glass chamber and kept there for 40 min under the ozone flow to increase the hydrophilicity and surface activity by introducing surface functional groups. In the end, nitrogen flow was introduced to replace the ozone gas and break the chain of functionalization [14].

2.2.2. Step II: Synthesis procedure of Pt-Ru (1:1 at. ratio) catalyst

The ozone-treated SWNTs were dispersed in i-PrOH by 15 min of Branson 3510 ultrasonication (room temperature, water-submerged, 100 W and 40 Hz). Pt and Ru were introduced during magnetic stirring, using a mixture of $H_2PtCl_6 \bullet 6 H_2O$ and $RuCl_3$ in ethanol as 1:1 at. ratio to synthesize Pt-Ru on SWNT. Dispersions were subjected again to 15 min of ultrasonication followed by an overnight stirring.

2.2.3. Step III: Procedure for decorating SWNT with Pt-Ru nanowires and nanoparticles

The well-dispersed catalyst ink, i.e. the dispersion of a catalyst material in i-PrOH with ratio of 1 mg/mL, was slowly heated in a tube furnace at a rate of 100 °C/h in N₂ gas atmosphere to remove the solvents and the counter ions, before switching to 5% H₂/Ar gas at 300 °C. The catalyst was kept at 300 °C for 2 h to reduce the Pt (IV) and Ru (III). After the heat treatment, the catalyst was cooled down to room temperature in N₂ atmosphere. The synthesis yield of the catalyst was ca. 89%.

2.3. MEA preparation

A 30 µm thick Fumasep® FAA-3–30 membrane (Fumatech) was ionexchanged in 0.5 M NaOH with stirring for 1 h and rinsed in Milli-Q water prior to cell assembly. The catalysts and Fumion® FAA-3 ionomer were mixed with H₂O and i-PrOH using a magnetic stirrer and Branson 3510 ultrasonication (room temperature, water-submerged, 100 W and 40 Hz). Both IrO_x and Pt-Ru (10 w-%) SWNT catalysts, the ionomer content was 25%. The anode catalyst loading was kept at 1.5 mg cm⁻² of IrO_x whereas the cathode catalyst loading was 0.034 mg cm⁻² of Pt-Ru (10 w-%) SWNT. The dispersions were painted by hand on GDLs using an airbrush (Badger NO 100 G) with nitrogen flow. The membrane was cut into a 46 mm diameter circular disc whereas catalyst coated GDL was cut into a 32 mm diameter disc, resulting in an active area of 8.04 cm².

2.4. Electrochemical measurements

2.4.1. Standard three-electrode cell

The electrochemical activity of the catalysts was measured using an Autolab potentiostat (PGSTAT128N, Metrohm Autolab B.V.) in a standard three-electrode cell with a catalyst coated glassy carbon (GC) disc (5 mm in diameter) as a working electrode, an Ir wire inside a compartment separated by sintered glass as a counter electrode, and a Hydroflex® reversible hydrogen electrode (RHE) as a reference electrode. The catalyst ink dispersed in i-PrOH with a loading of 0.2 mg cm⁻² was deposited on the GC disc electrode (0.19 cm²). Subsequently, 5 μ L of Nafion dispersion (25 μ L of 5% Nafion dispersion diluted in 1 mL of ethanol) was added on top of the catalyst layer as a binder. Polarization curves for HER were obtained using a linear sweep voltammetry from 0 to -0.4 V at 2 mV/s scan rate with step size 0.00488 V. All the measurements were performed in aqueous 0.1 M KOH electrolyte. The

measured electrodes were subjected to stability test at different current densities $(-1, -2, -5, -10, \text{ and } -20 \text{ mA cm}^{-2})$ and an Accelerated Stability Test (AST) for 5 000 cycles at 100 mV/s at a potential range of 0 to -0.4 V corresponding to ~ 12 h. After the tests, electrolyte was changed to a fresh one before recording the HER polarization curves. The electrochemical impedance spectroscopy was measured in potentiostatic mode at 0.35 V with an amplitude of 0.005 V from 100 kHz to 10 Hz. Ohmic electrolyte resistance (R_{el}) was estimated from the high frequency impedance in the non-Faradic region. The typical recorded value was $\sim 28 \Omega$ in the 0.1 M KOH solution. The EIS was measured in galvanostatic mode at -1, -2, -5, -10 and -20 mA cm⁻² from 100 kHz to 0.1 Hz.

2.4.2. AEM electrolyser cell

The electrolyser setup consists of a circular shape cell that has anode and cathode compartments separated by membrane electrode assembly (MEA). 0.1 M KOH is circulated in both compartments at 50 mL min $^{-1}$. The compartments consist of a titanium piston, a titanium mesh, and a titanium sinter. The MEA is placed between the sinters and the two sides are closed by tightening four screws to a torque of 1 Nm. To ensure the proper electrical contact between the cell parts, technical grade N₂ is applied to titanium pistons at 10 bar. The circulated 0.1 M KOH is heated by heat exchangers before entering to anode/cathode compartments. The cell temperature is measured at the outlet of 0.1 M KOH circulation which is set at 45 °C. The cell measurements were conducted using AUTOLAB PGSTAT302N potentiostat equipped with a Booster20A and Nova 2.1 software. The cell was left to stabilize for 1 h before starting any measurements. The polarization of the cell was measured potentiostatically starting at highest current density, 0.7 A cm⁻² and decreased subsequently to 0.1 mA cm⁻². After the polarization, potentiostatic impedance was measured at 500 mA $\rm cm^{-2}$ with 10% amplitude from 10 kHz to 10 mHz. The MEA (0.034 mg cm⁻² of Pt-Ru (10 w-%) SWNT and 1.5 mg cm⁻² of IrO_x) was tested at constant current mode at 0.5 A cm⁻². The temperature of the constant current operated cell was set at 45 °C. The hydrogen gas flow rate was measured at the H_2 vent port using volume displacement method. Using the same MEA preparation technique, PtRu 20% C (0.034 mg cm⁻² of PtRu) was also tested as a cathode against IrO_x (1.5 mg cm⁻²) as an anode at 45 °C.

2.5. Physical characterization

2.5.1. Scanning transmission electron microscopy (STEM)

To investigate the morphology of material using STEM, samples were dispersed in ethanol (conc. 0.01 mg/mL) and 10 μ L of that solution was dropped on holey-carbon Cu coated TEM grid (Agar Scientific). The grid was dried in ambient air and the images were taken using a JEOL-2200FS, double Cs-corrected HRTEM at an acceleration voltage of 200 kV. Additional characterization was conducted on a dedicated probe aberration corrected Nion UltraSTEM100 in near ultra-high vacuum (10⁻⁹ mbar), operated at acceleration voltage of 60 kV.

2.5.2. X-ray photoelectron spectroscopy (XPS)

XPS was used to study the chemical compositions of the catalyst materials. All X-ray photoelectron spectroscopy (XPS) measurements were acquired using a PHI Quantera II scanning X-ray microprobe operating with an Al K_{α} radiation source. The catalysts were demobilized on a vacuum proof double-sided tape (3 M) and the spectrum was acquired on a 200 µm diameter spot using 50 W and 15 kV electron and ion neutralizer respectively. Survey scans were obtained with a step size of 1 eV while 280 eV of pass energy was acquired for 200 ms dwell time per step. The high-resolution narrow scans with 0.125 eV steps at 140 eV pass energy were collected for 1000 ms dwell time per step. All data was analyzed using CasaXPS *V. 2.3.18* with instrument-specific relative sensitivity factors, Shirley type backgrounds, and a binding energy scale calibrated to the adventitious carbon peak at 284.8 eV.

2.5.3. Inductively coupled plasma mass spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (NexION 350x, PerkinElmer) was used to determine the metal loadings of electrocatalysts. The catalyst samples were weighed in porcelain crucibles and burnt for 3.5 h at 650 °C in air. The crucible with the residue was subsequently boiled in aqua regia. The acid was transferred into a 50 mL volumetric flask and the crucible was washed 3 times with water, which was also added to the flask. Lastly the flask was filled to 50 mL and further diluted in a 1:100 ratio. These dilutions were then measured to calculate the exact amount of Pt. The amount of Ru cannot quantify during the experiment as Ru is insoluble in aqua regia.

2.5.4. X-ray powder diffraction (XRD)

To investigate the crystal structure, X-ray diffraction was performed using a PANalytical X'PertPro diffractometer equipped with a Cu K_{\alpha1} X-ray source. The samples were measured on a standard zero background holder in a 20 range of 5°–100°. The raw data was shift-corrected and fitted using the LeBail analysis and the program FullProf.

2.6. Computational model

Spin-polarized DFT calculations was used to elucidate the contribution of nanowires and nanoparticles towards the HER activity. The calculations were carried out using the Vienna ab initio simulation package (VASP) within the generalized gradient approximation based on Perdew-Burke-Ernzerhof (GGA-PBE) functional (see Supporting Information), with van der Waals D3 correction by Grimme [25]. The details of the calculations and model systems are shown in the Supporting Information.

3. Results and discussions

The intratube-nanowires and surface-nanoparticles of Pt-Ru on single walled carbon nanotubes (SWNT) were synthesized by reducing a dispersion of SWNTs and metal salt precursors in 5% H₂ in Ar atmosphere at 300 °C (see the experimental section for details). For the synthesis, Pt and Ru in various atomic ratios with 5 wt% total metal loading were applied, while the compositions of the received materials, designated as Pt-Ru SWNT, were determined by inductively coupled plasma mass spectrometry (ICP-MS), (Table S1 in the Supporting Information). Prior to the Pt-Ru nanowires and nanoparticles synthesis, SWNTs were functionalized with ozone to introduce oxygen functional groups on the surface of SWNT as revealed earlier by XPS [14] to enhance the adhesion of ionic Pt and Ru precursors. With the same total metal mass loading (5 wt%), we found that the Pt and Ru with 1:1 at. ratio was electrochemically more active and selected it for further characterization to understand the nature of high activity (see Supplementary Fig. S1a). Similarly, Pt SWNT (5 wt% of theoretical Pt metal loading) and Ru SWNT (5 wt% of theoretical Ru metal loading) electrocatalysts were also synthesized as reference materials using the same procedure. The catalyst support effect was also evaluated by using SWNT and Vulcan carbon as support materials and we observed that SWNT based material is more active and stable (see Supplementary Fig. S1b) and hence a relevant support choice.

3.1. Structural characterization of Pt-Ru SWNT

Based on the electron microscopy investigations, nanocrystalline metal content in the Pt-Ru SWNT and Pt SWNT samples is partially encapsulated within the internal cavities of SWNTs and partially dispersed on their surface (Fig. 1). The (pseudo-)spherical particles visible in Fig. 1a-b are randomly dispersed and appear to be surface-bound, whereas the nanowire-like particles precisely follow the SWNT axis, and the shape likely results from atoms being kinetically trapped within the nanotubes' internal cavities. The encapsulated (intratube) nanowires exhibit either a body centered or face centered cubic (BCC/



Fig. 1. TEM and STEM analysis. (a-b) An overview and closeup STEM ADF images of suspended SWNT bundles decorated with Pt-Ru nanoparticles and intratubular nanowires. (c) An atomically resolved image of an intratube nanowire. (d) TEM image of the catalyst material with the corresponding electron diffraction image in (e). Some Pt lattice planes are indicated with circle overlays and with Miller indices. The arrows and small circles highlight two pairs of reflections that correspond to a *d*-spacing of ca. 2.68 Å. (f) Fourier transform of panel (c). The identifiable reflections (blue circles) correspond best to (110) lattice planes of a cubic symmetry (orange lines) and a *d*-spacing of 2.69 Å for Pt-Ru.

FCC) symmetry, whereas surface particles correspond generally best to an FCC structure. Atomically resolved annular dark field (ADF) images acquired with an aberration corrected scanning transmission electron microscope (STEM) of both morphologies are shown in Fig. 1b. The lattice parameters of the spherical particles (FCC) as measured from selected area electron diffraction (SAED) images are 3.99 \pm 0.04 Å both for the Pt SWNT and Pt-Ru SWNT samples. An example of a Pt-Ru SWNT SAED image and the location where it was recorded from are shown in Fig. 1e and d, respectively. Interestingly, although based on energy dispersive x-ray (EDX) spectroscopy, a Ru mass fraction of $12 \pm 7\%$ (mean and one standard deviation, see Supplementary Fig. S2) is detected in Pt-Ru SWNT samples, this appears to have only a minute effect on the lattice parameter. This is generally observed even though there are rather large local variations and in some areas the Ru concentration is as high as 25%. This result implies that only a small fraction of Ru used in the synthesis is alloyed with Pt.

The structure of the intratube nanowires, despite exhibiting a symmetry that is likely cubic, is significantly more difficult to accurately specify in the STEM/TEM experiments. Indeed, only the facet shown in Fig. 1c was observed in atomically resolved STEM experiments, which is believe to result from the momentum transfer from relativistic 60 keV electrons that align the wires along certain high symmetry directions that minimize the "electron wind" drag similar to a windsock [26]; the wires are kept in a certain orientation by only the weak van der Waals interactions that exist in between the wire and nanotube wall. By calculating Fourier transform (FT) of the atomically resolved STEM ADF images, a single *d*-spacing can be identified. This spacing appears to be present invariably but the value varies from 2.67 Å to 2.71 Å in different wires. An example FT is shown in Fig. 1f. While the observed value does not immediately correspond to any of the known d-spacing values of neither pure Pt or Ru phases, nor that of Pt-Ru alloys, it appears to occasionally be visible also in SAED images recorded in TEM (see for instance the diffraction spots marked yellow circles and arrows in Fig. 1e). If the nanowire's structure was purely cubic (i.e., either FCC or BCC), the only projection that produce the contrast visible in Fig. 1c would appear when the structure is viewed along the [111] zone axis. This would mean that the measured *d*-spacing of 2.69 ± 0.02 Å corresponds to the period of (110) lattice planes, and lattice parameter would therefore become 3.80 \pm 0.03 Å, which is by a factor of ca. 5% smaller than those of the surface pseudo-spherical particles.

Powder XRD analysis was used to identify the phases present in the Pt-Ru SWNT catalyst and Fig. 2a shows the measured XRD pattern of Pt-Ru SWNT. At least two sample-related phases can be detected for the alloy: an FCC lattice (*Fm*-3*m*), typical for metallic Pt and few additional Bragg reflections. As a comparison, pure Pt SWNT and Ru SWNT (for STEM images, see Supplementary Fig. S3) are also shown in Fig. 2a. Pt SWNT and the alloy are rather similar to one another: the former shows only FCC reflections with an extracted lattice parameter of 3.91



Fig. 2. (a) XRD patterns of the studied catalyst materials and the single crystal Si substrate, on which the sample was prepared (b) XPS analysis of the Pt-Ru SWNT catalyst compared with the Pt SWNT and Ru SWNT catalysts.

 \pm 0.01 Å, whereas Pt-Ru SWNT gives 3.93 \pm 0.01 Å (FCC), thus indicating a small amount of Ru has indeed entered the lattice even in the bulk. This is in a good agreement with the localized TEM diffraction measurements from which 3.99 \pm 0.04 Å lattice parameter (FCC) is estimated. Using the lattice values from XRD and the ICDD reference data for similar alloys, one can interpolate the presence of about 5–8% of Ru in the Pt-dominating FCC lattice, which is in agreement with the EDX analysis (see Supplementary Information). The difference in the absolute values is likely to be explained by the locality of the EDX method and, depending on the area where the data was recorded. The Ru SWNT sample appears to be X-ray amorphous (see Fig. 2a), most likely resulting from the small particle size [27].

To further understand the crystal composition of Pt-Ru SWNT, focus is paid on the additional reflections, the most unidentified reflection appears at 2.52 Å. In more careful examination, a small Bragg reflection is observed at 20 ~ 35.5° (X-ray $\lambda = 0.15406$ nm), not explained by known Ru, Pt-Ru or Fe phases (Fe acts as a minor impurity in the SWNTs). Despite multiple efforts to fit this reflection utilizing the observations from TEM and STEM, no unambiguous result was obtained to explain its origin. Thus, it must be concluded the phase(s) present are best understood by the details of the electron microscopy analysis.

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of Pt and Ru (see XPS, Fig. 2b) and the elemental composition (see Table 1). The fact that the atomic ratio of Ru based on the surface specific technique (XPS) is < 0.5 (as expected based on the synthesis) in comparison to the XRD results, suggests that Pt is enriched on the surface. Fig. 2b shows the Pt 4 f and Ru $3p_{3/2}$ regions of spectra for Pt-Ru SWNT, Pt SWNT and Ru SWNT. Based on the high-resolution spectra of Pt-Ru SWNT, Pt species are mostly metallic (71.2 eV), while Ru species are oxidized (463.2 eV) in the bimetallic catalyst. Similarly, Ru SWNT shows a shift corresponding to RuO₂. The Pt SWNT catalyst exhibits the same peak splitting (3.2 eV) as Pt-Ru SWNT but is shifted to slightly higher binding energies (72.1 eV) [28]. This shift can be either

Table 1

Elemental composition of Pt and Ru in the synthesized electrocatalysts from the XPS analysis.

Sample	Ru [at%]	Pt [at%]	Ru/Ru+Pt	C [at%]	O [at%]
Pt-Ru SWNT	0.04	0.13	0.235	96.81	2.95
Pt SWNT	0.00	0.29	0.00	93.92	5.74
Ru SWNT	0.33	0.00	1.00	95.09	4.28

due to particle size effects of the clusters [29] or to the formation of Pt oxides at higher binding energies of 72.4 -75 eV. The C 1 s and O 1 s XPS spectra are similar for all samples since they originate from the identical carbon support and adventitious carbon species.

3.2. Electrocatalytic performance of Pt-Ru SWNT

The electrocatalytic activity for the HER was evaluated by liner sweep voltammetry (LSV) in H2-saturated 0.1 M KOH in a threeelectrode electrochemical half-cell setup (see experimental section for details). Fig. 3a shows the LSV curves (iR compensated) of the synthesized Pt-Ru SWNT, Pt SWNT and Ru SWNT catalysts with intratubenanowire and surface-nanoparticle structures. Their HER activities are compared to those of commercials PtRu 20% C (20 wt% Pt Ru on Vulcan carbon in 1:1 at. ratio) and Pt 20% C (20 wt% Pt on carbon black). The Pt-Ru SWNT catalyst exhibits a zero onset overpotential comparable to the commercial catalysts. The overpotential at a certain cathodic current density is another important parameter to evaluate the electrocatalytic activities. Fig. 3b gives an overview of Pt to Ru ratio vs overpotential (η) at 10 mA cm⁻². Pt-Ru SWNT can achieve an HER current density of -10 mA cm^{-2} at an overpotential of 46 mV, requiring only 4 mV higher potential than the commercial Pt 20% C (42 mV) and 16 mV than the commercial PtRu 20% C (30 mV). A comparison of Pt-Ru SWNT with similar catalysts reported earlier is summarized in Table S2 (see Supplementary Information) showing that Pt-Ru SWNT compares favorably with other low-Ru and PtRu nanoclusters catalysts.

The electrochemical active surface area (ECSA) is used to evaluate the number of active sites available for the HER electrocatalyst. The ECSA values are obtained by COad stripping analysis assuming that the adsorbed CO adlayer (number of CO molecules per metal surface atom) is identical to the Pt and Pt-Ru surfaces with a charge density of 420 µC \mbox{cm}^{-2} [30]. Fig. 3c shows that the \mbox{ECSA}_{CO} values normalized to total PGM loading for Pt-Ru SWNT, Pt SWNT, PtRu 20% C and Pt 20% C, are 52.6, 51.7, 138 and 68.1 $m^2 g^{-1}$, respectively. The close correspondence between ECSA_{CO} values of the synthesized and commercial Pt catalysts suggest complete utilization of the surface-nanoparticles for the SWNT supported catalysts, while the intratube-nanowires are hypothesized to stay inactive to CO adlayer. In case of commercial PtRu 20% C, the increase in ECSA_{CO} with increasing Ru content may partly be attributed to the lower atomic mass of Ru as compared with Pt, which leads to higher number of metal (atom) surfaces for similar loadings [31]. Moreover, different particle size distribution among commercials PtRu 20% C (1.5



Fig. 3. (a) Polarization curves (iR compensated) and (b) the corresponding comparisons of overpotential obtained at a current density of -10 mA cm^{-2} . (c) CO stripping curves and ECSA_{CO} of the catalysts (normalized with metal mass) and (d) LSV normalized by ECSA_{CO}. All polarization curves were measured in H₂-saturated 0.1 M KOH with a catalyst loading of 200 µg cm⁻² at a scan rate of 2 mV/s.

 \pm 0.33 nm) and Pt 20% C (2.49 \pm 0.63 nm) is evident based on TEM images (see Supplementary Fig. S4), which also explains the difference observed between the ECSA_{CO} values.

Further, the HER current densities of the catalysts were normalized by ECSA_{CO} (see Fig. 3d) and active metal mass (see Supplementary Fig. S5). Fig. 3d shows that a low overpotential is required for Pt-Ru SWNT (~24 mV) to reach $-1 \text{ mA cm}_{\text{ECSA}}^{-2}$ in comparison to PtRu 20% C (>100 mV) and Pt 20% C (~78 mV). This suggests the chemical nature of the metal (in the commercial catalysts) is not important and the HER activity rather depends on the available sites. A plausible reason behind the higher HER activity of Pt-Ru SWNT is the availability of the intratube-nanowires to promote the HER, which tend to be inactive to CO adlayer in ECSA_{CO} [32]. Thus, both the noble metal intratube-nanowires and surface-nanoparticles of the synthesized Pt-Ru SWNT catalyst contribute towards HER catalysis (as discussed in the context of the computational results below). Fig. S5 (Supplementary Information) shows the LSV curves normalized by the theoretical Pt and Ru metal loadings further confirming the greater activity of Pt-Ru SWNT over the commercial catalysts. These results advocate that the use of extremely low loading of Pt-Ru with high aspect ratio to promote the HER in alkaline media is feasible.

The electrocatalytic durability was studied using accelerated stress tests (AST). Repeated cycling in the range from 0 to -0.4 V_{RHE} for 5 000 cycles was performed in 0.1 M KOH at a scan rate of 100 mV/s corresponding to 8 s per cycle and a total AST length of ~11 h. Fig. 4a demonstrates the HER activity of Pt-Ru SWNT before and after the AST,

where a negligible change in the activity indicates good durability. Small decrements in the activity are common due to loss of material under these experimental conditions (rotation and gas bubble evolution). Throughout the potential range where H₂ bubble formation is moderate enough to maintain the curves linear and comparable, the potential loss is no more than 5 mV after 5 000 cycles for Pt-Ru SWNT. In case of the commercial catalysts, the potential loss is clearly higher, 10 mV or more, after the AST (see Supplementary Fig. S6). The size distributions of Pt-Ru features before and after AST was studied with TEM imaging as shown in Fig. 4c. Under potential cycling in alkaline conditions, the morphology and structure of the intratube-nanowires and surface-nanoparticles are well-retained after the AST. The values extracted from histograms represent the mode of distribution, meaning the maximum of log-normal probability density function with 95% confidence interval in the parenthesis. The size of the surfacenanoparticles does not change significantly after the cycling, and the bulk of nanoparticles are still in range of 1.2 nm (0.8–1.6). This is quite interesting as smaller particles tend to agglomerate faster under similar conditions. However, functionalization of SWNTs increases the adhesion of nanoparticles which prevents their migration [33,34]. In our work, SWNTs are pre-treated with O3 which explains the results. The intratube-nanowires have not experienced any drastic degradation as the width, 0.6 nm (0.4-0.8), and length, 4.0 nm (2-6), distributions remained almost unaffected during the AST. The specific surface area is calculated assuming that the intratube nanowires are perfect cylinders and the surface nanoparticles are perfect spheres. The corresponding total specific surface area is 127 $m^2 g^{-1}$ and 128 $m^2 g^{-1}$ before and after



Fig. 4. (a) Polarization curves of Pt-Ru SWNT before and after an accelerated stability test (AST) and (b) chronopotentiometry of Pt-Ru SWNT at different HER current densities. All measurements are iR compensated and measured in H₂-saturated 0.1 M KOH electrolyte with a catalyst loading of 200 μ g cm⁻². (c) STEM images (dark field) and corresponding particle size distributions of Pt-Ru SWNT before and after the AST.

the AST, respectively. The nanowires contribute to the specific surface area of 74 m² g⁻¹ and 70 m² g⁻¹, while the nanoparticles retained the specific surface area of 54 m² g⁻¹ and 58 m² g⁻¹ before and after the AST. The nanowires have clearly a higher contribution to the total

specific area than the spheres even though they contain 44% of the metal in mass. Consequently, a higher specific activity is expected to be reached with a higher concentration of the nanowires.

The chronopotentiometric response of the Pt-Ru SWNT



Fig. 5. (a) Tafel plots obtained from the polarization curves and (b) Nyquist plots of the measured EIS for Pt-Ru SWNT at different HER current densities with the equivalent circuit used for the data fitting. The data is marked with circles (\circ) and the fits with a line and crosses (\times).

electrocatalyst at different current densities were tested for a total of 100 min (see Fig. 4b). The corresponding potential for Pt-Ru SWNT shows a linear trend at low current densities indicating long-term stability of Pt-Ru in alkaline media, being ascribed to the good stability of Pt-Ru SWNT. In the earlier work by Rajala et al. [14], the chronoamperometric measurement have shown a comparable stability with our results for Pt nanowires on SWNT in acidic medium, whereas the catalyst activity has been observed to decrease significantly for pseudo-atomic-scale Pt on SWNT by Tavakkoli et al. [24]. However, unstable chronometric profile is recorded here for Pt-Ru SWNT at high current densities ($\leq -10 \text{ mA cm}^{-2}$) due to vigorous evolution of H₂ bubbles.

First insight on the HER mechanism is received from Tafel slopes, which are generally used to determine the rate determining step in the HER. Tafel plots derived from the polarization curves of the synthesized catalysts are shown in Fig. 5a. Pt-Ru SWNT results in a Tafel slope of 36 mV dec $^{-1}$ (n = 46 mV) compared to Tafel slopes of 42 and 38 mV dec⁻¹ for Pt SWNT and Ru SWNT, respectively. The low Tafel slope of 36 mV dec⁻¹ for Pt-Ru SWNT suggests that this material catalyzes the HER through the Volmer-Heyrovsky mechanism in which a fast electrochemical discharge step (Volmer reaction, $H_2O + e^- \rightarrow H_{ads} + OH^-$) is followed by an electrochemical desorption step (Hevrovsky reaction, $H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$) while the desorption of hydrogen is the rate limiting step. The HER exchange current densities (j₀) for Pt-Ru SWNT, Pt SWNT and Ru SWNT, estimated from the Tafel plots by extrapolation, are 0.66, 0.52 and 0.44 mA cm^{-2} respectively. In case of commercial PtRu 20% C and Pt 20% C, the estimated exchange current densities are slightly higher 0.70 and 0.68 mA cm^{-2} , respectively [35, 36]. With these values correlating closely to exchange current density obtained for the Pt-Ru SWNT electrocatalyst.

Electrochemical impedance spectroscopy (EIS) was used to further study the HER kinetics on Pt-Ru SWNT at four different current densities $(-2, -5, -10 \text{ and } -20 \text{ mA cm}^{-2})$ depicted in the form of a Nyquist plot. The data is interpreted to be caused by a resistor (Rel) and an RC-circuit (R_{ct} and C) according to the equivalent circuit shown in Fig. 5b. Rel results from the ohmic resistances of the system covering the electrolyte, the catalyst layer, and the connections of the system. The RC-circuit is caused by the HER and forms a semi-circle in the low frequency region. The values of the fitted key parameters for Pt-Ru SWNT and PtRu 20% C at different current densities are represented in Fig. S7 (see supplementary information). The difference in charge transfer resistance (R_{ct}) on Pt-Ru SWNT and PtRu 20% C is declined towards high current densities. R_{ct} decreases with current as the loss of the electrochemical reaction decreases due to the faster reaction kinetics. In addition, capacitance (C) decreases with the current which can be explained by the fact that with high reaction rate more active sites are blocked by the evolution of gas bubbles [37]. Therefore, C of Pt-Ru SWNT is decreased at high current densities due to different porosity and hydrophilicity of the catalyst support and location of the catalyst particles. Unfortunately, the EIS data is quite unstable at high current densities because of vigorous H₂ bubble formation which makes the potential unstable (see Fig. 4b). Consequently, the quality of the data is poor and fitting difficult.

3.3. First-principles density functional theory (DFT) calculations

First-principles calculations based on density functional theory (DFT) including the Grimme D3 dispersion corrections [25] were conducted to shed light into the activities of these systems towards HER. The Me-SWNT structures (Me = Ru, Pt-Ru, and Pt) were modelled by embedding the Me nanowires within a (12,12) armchair SWCNT as shown in Fig. 7a and b (for the cases of Pt SWNT and Pt-Ru SWNT, respectively). Each supercell (enclosed by solid black lines) is composed of 96 carbon atoms and 54 metal atoms. A larger (14,14) armchair carbon nanotube (CNT) comprising of 112 C atoms per supercell is found to not interact directly with the embedded metal nanowire as the

C and Me orbitals remain sufficiently far off to prevent the charge densities to interact, thus not further studied for this reason; in contrast, the charge density plots of a CNT with 96 C atoms per supercell encapsulating the metal nanowire provide sufficient bonding interaction between the metal and carbon atoms of the nanotube (Fig. S8). For Pt SWNT, the metal nanowire inside the SWNT follows a close-packed ABAB stacking to fit the dimensions of the nanotube with, similar to our STEM observations, an FCC(111)-like plane facing perpendicular to the axis of the tube. The calculation of the formation energies shows that such configuration for Pt SWNT shows a higher stability than for a Pt nanowire with a BCC-like structure by 2.73 meV/atom (Fig. S9). In contrast, the BCC-like structure appears to be more stable than the close-packed ABAB stacking for the case of Ru SWNT (Fig. S10). Ru is known to have an HCP bulk crystal structure, which is different from the FCC structure of Pt [38]. For the Pt-Ru SWNT system, a comparison of several Pt and Ru atom distributions with a Pt:Ru ratio of 1:1 found that a Pt-enriched surface of the nanowire with a BCC-like structure is more stable than a solid solution of Pt and Ru and the close-packed ABAB stacking (Fig. S11). Because of the difference in the atomic radii of Pt and Ru, such structure provides an optimized distribution of metals inside the SWNT. This is consistent with the earlier mentioned elemental composition (Table 1) from the surface specific XPS, which indicate the enrichment of the surface by Pt. This also agrees with the theoretical prediction of Ruban et al.[39], which found that a Pt solute has a very large tendency to surface segregation on Ru.

Meanwhile, the surfaces of the Pt and Pt-Ru nanoparticles were modelled using (111) slabs with four atomic layers, vacuum height of ca. 12.0 Å, and supercell sizes shown in Fig. 6c and d. Slab models are widely used to model the surfaces of the nanoparticles [40,41]. Pt(111) is known to be the stable surface facet of a Pt nanoparticle and is usually selected as a prototype for experiments and theoretical studies [42]. The Pt-Ru alloy was modelled by a Pt-monolayer pseudomorphically laid on a homogeneous 1:1 FCC Pt-Ru alloy as shown in Fig. 6d, which will be referred in the manuscript as Pt(111)/Pt-Ru. Such FCC lattice structure for a bulk Pt-Ru has been found experimentally in an annealed polycrystalline Pt-Ru and has thus been used in other DFT studies [43]. This is also consistent with the XRD data for catalysts with platinum (Pt-Ru SWNT and Pt SWNT) in Figs. 2a and 1e, which found the reflections for indices characteristic of an FCC crystal. The calculated surface energies show that such model of a Pt monolayer on a Pt-Ru alloy is more stable by 52.2 meV/Å² compared to a homogeneous Pt-Ru solid solution (Table S3). This is in agreement with the earlier noted very strong segregation tendency of Pt on Ru based on a previous DFT calculation [39] and the observed Pt enrichment of the surface based on the XPS measurements (Table 1). Moreover, a similar Pt skin on Ru has been used by Li and co-workers [41] to model the adsorption of H on Pt-Ru alloys.

The calculated bulk lattice constants of FCC Pt and Pt-Ru are 3.92 Å and 3.82 Å, respectively, in agreement with the above presented STEM/ TEM experiments (Fig. 1) and with earlier experiments by others [44], and with earlier DFT studies [43,45]. Table S4 shows the coverage dependence of hydrogen adsorption energies on a Pt(111) surface. An adsorbed hydrogen coverage of 0.25 mL was chosen for both Pt(111) and Pt(111)/Pt-Ru for consistency, which has also been used in other DFT studies for HER on Pt(111) [41,46]. Notably, a bilayer model for a Pt skin on transition metals has been previously found to have similar properties to pure Pt and is thus not used in this study [47].

The adsorption site of a hydrogen adatom (H*) was confirmed by comparing its adsorption energies at different positions on the catalysts. As shown in Fig. 6a and b, H* resides on top of C, with C–H bond lengths of 1.200 Å, 1.113 Å, 1.115 Å and 1.115 Å for SWNT, Ru SWNT, Pt SWNT and Pt-Ru SWNT, respectively. On the other hand, Fig. 6c shows that H adsorbs at the FCC hollow site of Pt(111), with a Pt–H distance of 1.86 Å. This agrees with other DFT studies that utilized different exchangecorrelation functionals and dispersion corrections [40,41,46]. Interestingly, H* resides at the top site of the Pt-Ru alloy (Fig. 6d), with a Pt–H



Fig. 6. The adsorption configurations of H* on a) intratube Pt SWNT b) intratube Pt-Ru SWNT, c) Pt(111) and d) Pt(111)/Pt-Ru. For parts c and d, the right and left panels show the top and side views of the surfaces. The solid black lines show the size of the supercell, which corresponds to a H* coverage of 0.25 mL for the metal slab models.

bond length of 1.58 Å. The preference of H* to reside on the top site of Pt-Ru can be attributed to its weaker adsorption on Pt-Ru than on Pt, as will be presented later. Such weak interaction between Pt and H on the surface of Pt-Ru is optimized when H* resides on the top site, which provides the shortest Pt–H bond length. By comparison, H adsorption at the FCC hollow site of Pt-Ru is 0.044 eV less favorable than on the top site.

It is widely accepted that the Gibbs free energy for hydrogen adsorption ΔG_{H^*} can be used as a major descriptor for the HER activities of various catalysts [46]. It is calculated as:

 $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S$

where ΔE_{H^*} , ΔE_{ZPE} , and $T\Delta S$ are, respectively, the adsorption energy of hydrogen, and the difference in the zero-point energy and entropy between the adsorbed hydrogen and hydrogen in the gas phase. The entropy of a gas phase hydrogen includes the translational, rotational, and vibrational components, evaluated at T = 300 K and P = 1 atm. The values of these are reported in Table S5. A value of ΔG_{H^*} that is close to zero (thermoneutral) suggests a good catalyst for the HER, as noted in volcano plots for HER activities on various catalysts [46]. Fig. 7 shows



Fig. 7. The 3-state free energy diagram for HER. The coverage of H^* on Pt(111) and Pt(111)/Pt-Ru is 0.25 mL.

the 3-state free energy diagram for HER on the Me-SWNT systems and slab models (Pt and Pt-Ru). For the Me-SWNT systems, the predicted HER activities are in the order of Pt-Ru SWNT > Ru SWNT > Pt SWNT, in excellent agreement with the polarization curves for current densities $> -4.0 \text{ mA cm}^{-2}$ (Fig. 3a) and normalized LSV (Fig. 3d) presented earlier. It can be noted that the ΔG_{H^*} for a pure carbon nanotube (denoted as "SWNT" in Fig. 7) has a large positive value, which indicates that H adsorption on this system is highly unfavorable. This is consistent with other studies, which show that the adsorption of hydrogen on a pristine carbon nanotube is very weak [48,49]. The magnitudes of ΔG_{H^*} for the Pt-Ru SWNT and Pt-Ru slab have comparable values of 0.12 eV and 0.13 eV, respectively. However, the different signs of ΔG_{H^*} indicate the difference in the HER mechanism on these two surfaces. For the Pt-Ru SWNT, HER is limited by the endothermic H* adsorption, while for the Pt-Ru slab, HER is limited by the release of H2 gas. The generally lower HER activity of Pt SWNT compared to Pt-Ru SWNT shown in Fig. 3a and d is due to the strong adsorption of H* on the Pt SWNT shown in Fig. 7 and Table S5. On the other hand, the weaker adsorption of H* (i.e., ΔG_{H^*} is closer to zero) on Pt-Ru SWNT compared to Pt SWNT suggests a faster formation and release of molecular hydrogen.

The Pt(111)/Pt-Ru slab model promotes a more favorable ΔG_{H^*} for HER than the Pt(111) slab, in excellent agreement with polarization curves in Fig. 3a, which shows PtRu 20% C to have higher HER activity compared to Pt 20% C. This agrees with a previous DFT study, which have shown that the Pt-Ru alloys (modeled using a single and double Ptdopant and Pt-skin on a Ru(101) surface) promote a lower magnitude of ΔG_{H^*} than the monometallic Pt(111) [41]. To shed light into the weaker adsorption of H* on Pt-Ru compared to Pt, the local density of states (LDOS) projected on a surface Pt atom of the monometallic Pt and bimetallic Pt-Ru slab models are shown in Fig. 8. It is noted that with respect to the monometallic Pt(111), the surface Pt atoms in the model Pt monolayer on Pt-Ru(111) are compressed by 2.55%. Moreover, Bader charge analysis found that a surface Pt atom on the Pt-Ru model slab has gained 0.11 eV from the subsurface Ru. This combined geometric and electronic effect is characterized by the downshifting of the Pt d-band in the Pt(111)/Pt-Ru model system compared to the monometallic Pt, as shown in Fig. 8. Correspondingly, the position of the d-band center of the surface Pt atom on Pt-Ru is shifted further away from the Fermi level compared to the pure Pt case (dashed lines in Fig. 8). Based on the d-band center model, such downward shift in the metal d-band will result in the lower electron occupancy of the sp-d antibonding orbital upon the adsorption of a molecule, thereby weakening its adsorption on the surface.



Fig. 8. The local density of states (LDOS) projected on the surface Pt atom of the monometallic Pt(111) and the model Pt monolayer on Pt-Ru(111). The vertical dashed lines show the positions of the Fermi energy (black), and the positions of the d-band centers for Pt(111) (blue) and Pt monolayer on Pt-Ru (111) (red), with values of -2.61 eV and -3.14 eV, respectively.

3.4. AEM electrolyser test

Inspired by the improved HER performance and good stability of the Pt-Ru (5 w-%) SWNT (10 μ g cm⁻² of metal loading) catalyst, we wanted to test the catalyst material in an AEM electrolyser as a two-electrode configuration (see for details the experimental section). Using thinner electrodes with the same total Pt-Ru loading is beneficial for the overall

electrolyser performance as this results in lower mass transfer losses in the electrodes [50]. Hence, we also wanted to investigate if the metal content can be increased without losing the mass activity. According to Fig. 9a, HER mass activity is slightly decreased when increasing the metal content from 5 wt% to 10 wt% but radically reduced when metal content is increased to 15 wt%. Apparently, particles concentration per functional site on the SWNT support is reaching saturation with higher Pt-Ru loadings. Thus, solely increasing the metal loading above 10% does not increase the HER activity as significantly anymore.

Therefore, we selected 10 w-% (see Supplementary Fig. S12) for the electrolyser test. The polarization curve, long-term measurement at constant current and impedance are analyzed as shown in Fig. 9. From the polarization curve, Fig. 9b, the cell achieves industrially required current density as high as 500 mA $\rm cm^{-2}$ at an ultralow cell voltage of 1.72 V ($34 \mu g \text{ cm}^{-2}$ of metal loading). This overpotential at 500 mA cm^{-2} is equivalent to the one recently reported by Zhai et al. [51] (Ru₁/D-NiFe LDH, 1 M KOH). However, the activity of the Pt-Ru SWNT electrode can even be considered higher when taking into account the lower molar concentration of the electrolyte and electrode loading, indicating the promising potential of the catalyst studied here. Faid et al. [52] reported the overpotential of 1.65 V for a Pt/C cell at the same current density at 50 °C with a far higher cathode loading. The commercial PtRu 20% C is also measured as a cathode catalyst using the similar metal loading (34 μ g cm⁻²) as for Pt-Ru SWNT. The cell achieves the current density of 170 mA cm⁻² at cell voltage of 1.9 V (see Supplementary Fig. S13), which is a poor performance in comparison to the investigated Pt-Ru SWNT catalyst. During the constant current



Fig. 9. (a) Polarization curves (*iR* compensated) normalized by theoretical total mass of Pt and Ru performed in H₂-saturated 0.1 M KOH electrolyte with catalyst loading of 200 μ g cm⁻² in a three-electrode RDE setup. AEM electrolyser measurements of Pt-Ru (10 wt%) SWNT as a cathode depicting (b) polarization curves with *iR*-free voltage, (c) constant current operated, and (d) impedance of the full cell. The cell was operated at 45 °C with 0.1 M KOH electrolyte feed using a Fumatech FAA-3 membrane painted with 34 μ g cm⁻² of cathode total metal and 1500 μ g cm⁻² of anode IrOx loading.

experiment of Pt-Ru SWNT, Fig. 9c, the MEA is stable until 24 h at a constant voltage 1.80 V. The H₂ production rate is 29.4 mL min⁻¹ which equals to 97.7% Faradic efficiency for HER at a current density of 0.5 A cm⁻². The small difference from 100% can be due to inaccuracy of the measurement method or hydrogen cross-over considering FAA-3 membranes are thin (30 μ m). The voltage starts to drop suddenly after 24 h while the hydrogen evolution stops. This is ascribed to the short circuiting of the cell because of the membrane breakage. In terms of the lifetime, a similar FAA-3 membrane has been earlier reported to fail within 31 h [53].

4. Conclusions

In summary, a simple and scalable synthesis process is described for an intratube high aspect ratio/low-loading Pt-Ru SWNT catalyst. Based on the Pt-Ru intratube-nanowires and surface-nanoparticles active sites, Pt-Ru SWNT achieves higher HER performance in alkaline medium with low-overpotential, high current density and long-term durability. The Pt-Ru SWNT catalyst exceeds both commercial PtRu 20% C and Pt 20% C, as references, in mass normalized HER activity. In addition, Pt-Ru (10 wt%) SWNT is a promising cathode catalyst in an AEM electrolyser based on the stability (at least 24 h) and the activity approaching to a commercial Pt/C cathode catalyst at very low loadings of precious metals (34 μ g cm⁻²). The well-defined intratube-nanowires and surfacenanoparticles structures of the catalyst also allow for fundamental investigation of HER kinetics in an alkaline electrolyte. The DFT calculations reveal that our Pt-Ru intratube catalyst promotes weaker adsorption of H* and thus facilitates higher rates of H₂ formation. This work not only develops a simple synthesis process of Pt-Ru SWNT catalyst but also computationally and experimentally confirms the central role of intratube-nanowires in electrocatalytic activity and stability, opening new possibilities for the development of less costly commercial AEM electrolyser.

CRediT authorship contribution statement

Farhan S. M. Ali: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. Ryan Lacdao Arevalo: Methodology, Formal analysis, Investigation, Writing – review & editing. Matthias Vandichel: Methodology, Formal analysis, Investigation. Florian Speck: Investigation, Writing – review & editing. Eeva-Leena Rautama: Formal analysis, Writing – review & editing. Hua Jiang: Investigation, Writing – review & editing. Olli Sorsa: Formal analysis, Writing – review & editing. Kimmo Mustonen: Formal analysis, Investigation, Writing – review & editing. Serhiy Cherevko: Supervision, Writing – review & editing. Tanja Kallio: Conceptualization, Methodology, Supervision, Writing – review & editing, Resources, Data curation.

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Conflict of interest

Authors have no financial/commercial conflict of Interest or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.121541.

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