

Turbast aktiveeritud eriomadustega süsiniku tootmine elektrokeemilistesse seadmetesse

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Turbavarud Eestis

- Maailma turbarabad sisaldavad umbes 550 gigattonni süsinikku
- Eestis Põhja-Euroopas rikkalikumad varud: 22% (~1 miljon ha) Eesti territooriumist on kaetud soode ja rabadega
- 300 registeeritud maardlat
- Aastatoodang ~1 miljon tonni (lubatud tootmismahd 2,6 miljonit tonni)
- Kasutatakse põhiliselt energiaallikana kombijaamades, aianduses
- Eesti turbad jaotuvad: hästilagunenud , mõõdukalt ja vähelagunenud turbaks;
keemiliselt neljaks klassiks: bituumenturvas, karbohüdraatne , ligniinturvas ja humiinturvas

Uuriti kahe erineva turba kasutusvõimalusi:

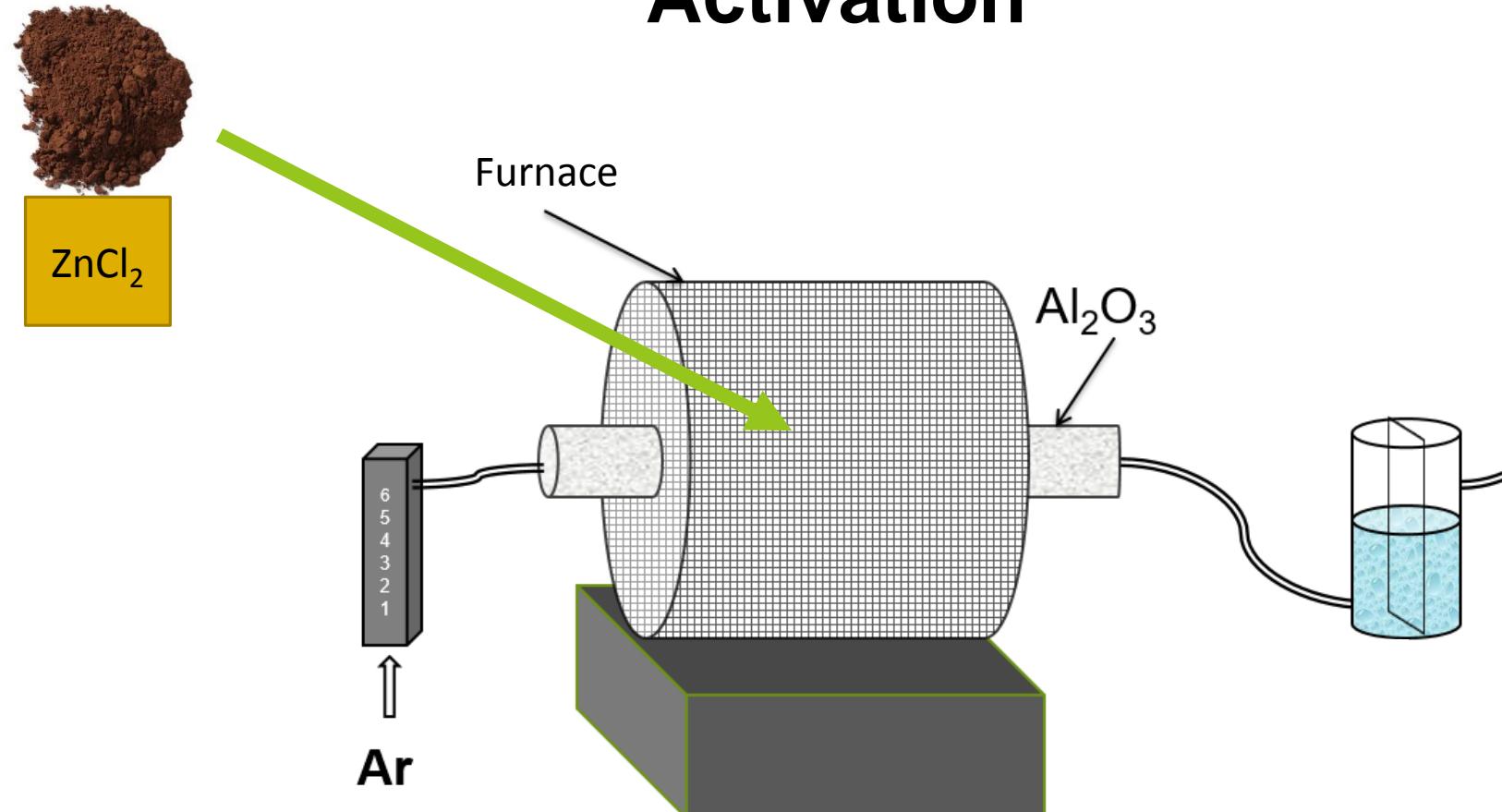
- Vähelagunenud turvas- Keressaare soo (AS Tartu Jõujaam)
- Hästi lagununud (nn mudturvas) - Möllatsi maardla (soo) (AS Tartu Jõujaam)
- Sobivamaks osutus hästi lagunenud turvas

Sünteesi käik.

Detailid: M.Härmas, et. al., *J Applied electrochem.* 2019. <https://doi.org/10.1007/s10800-019-01364-5d>

- Turba blenderdamine (peenendamine ja kuivatamine)
- Pürolüüs 450 kuni 800 °C juures (temperatuuri tõstmise kiirus 5 °C/min)
- Süsiniku puhastamine mineraalsooladest ehk pesu
 - HCl-i lisamisel happelises keskkonnas ($\text{pH} \sim 1$) 12h ($T = 60^\circ\text{C}$)
 - 20% KOH lahusega 2t ($T = 70^\circ\text{C}$)
- Filtreeritud Milli-Q veega, kuivatamine vaakumahjus (50 mbar / 80 °C)
- Leotatud ja loputatud Milli-Q veega 12h
- Filtreeritud ja vaakumahjus kuivatatud (50mbar / 80 °C)
- Edasi pürolüüs fikseeritud temperatuuridel alates 1000 kuni 1600 °C juures (T kasvukiirused erinevad (2- 4 °C/min))

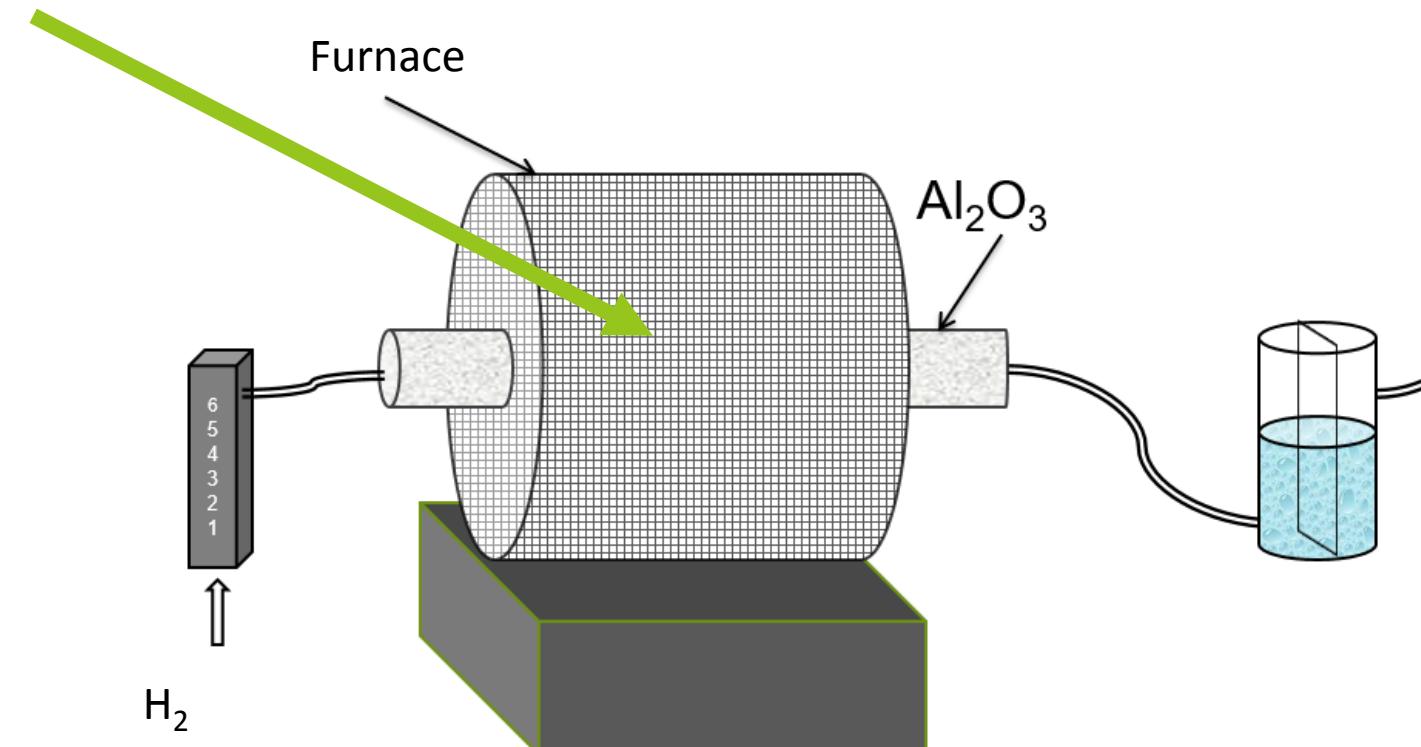
Synthesis: step 2 Activation



$700\text{ }^{\circ}\text{C}, 2\text{ h}, 5\text{ }^{\circ}\text{C min}^{-1}$

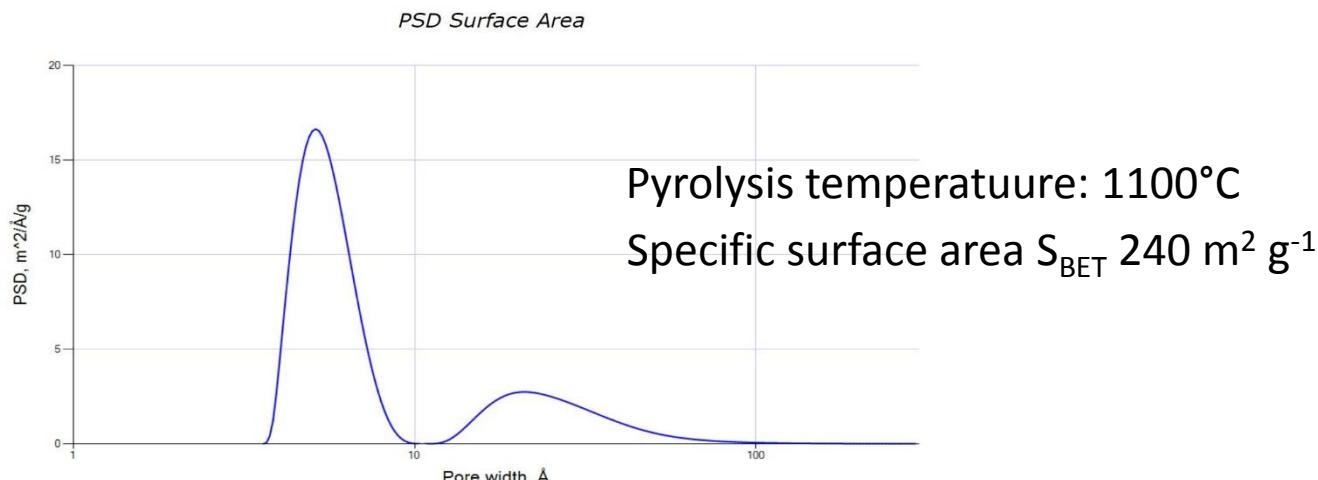
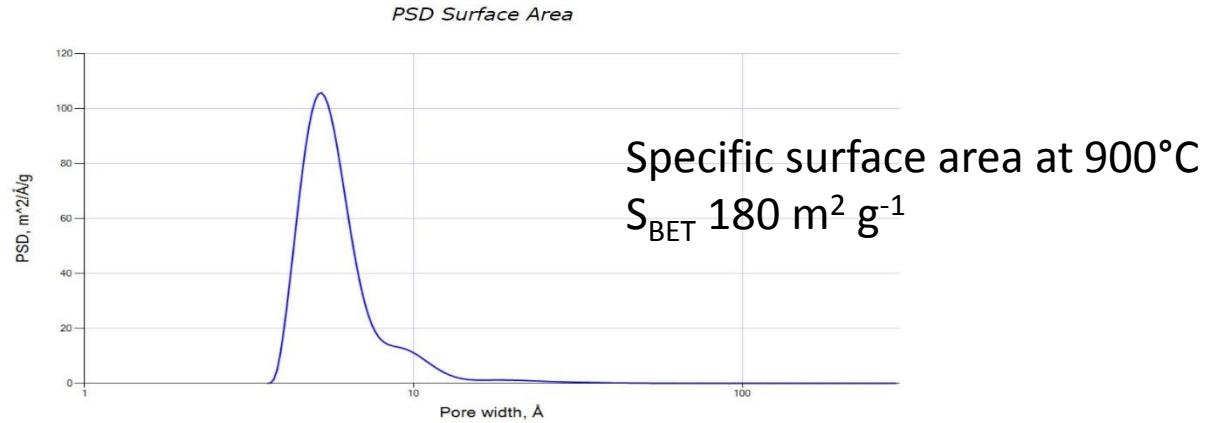


Synthesis: step 3 H_2 reduction



900 °C, 1 h, max °C min⁻¹

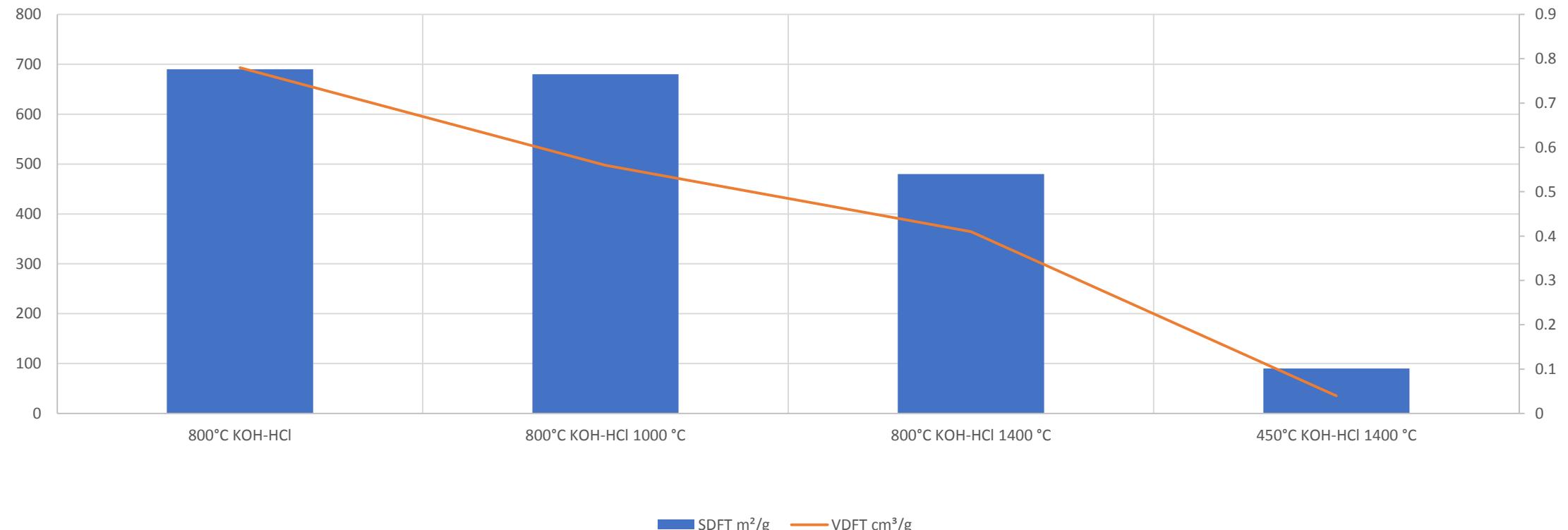
Pore size distribution by surface area

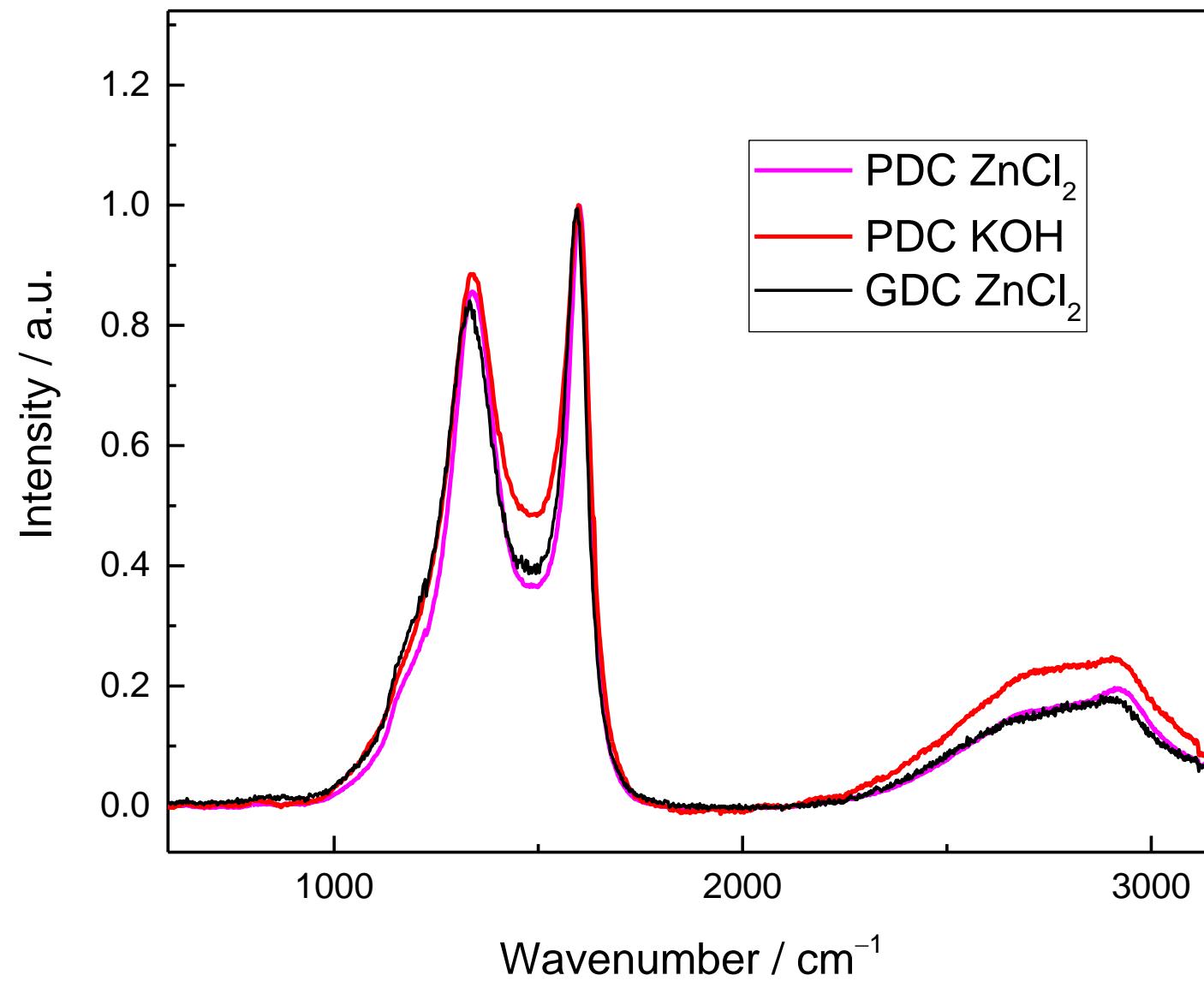


- Meso pores formation started at $T = 1173$ K.
- Mesopores are inevitable for high energy density devices!
- Same materials demonstrated specific surface area values $S_{BET}=1000$ m²/g or higher!

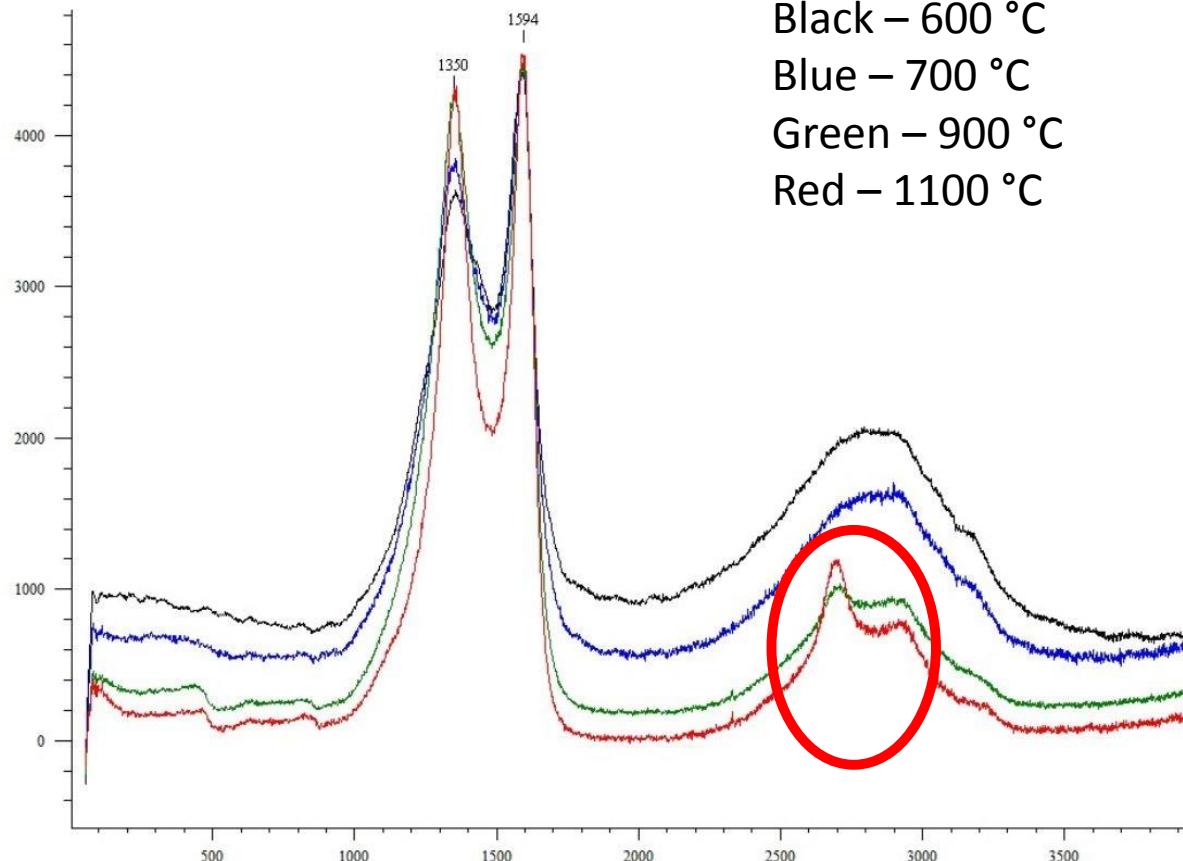
Materjal	N2						CO2		N2+CO2	
	SBET	SDFT	Vtot	VDFT	Smicro (t-plot)	Vmicro (t-plot)	SDFT	VDFT	SDFT	VDFT
	m ² /g	m ² /g	cm ³ /g	cm ³ /g	m ² /g	cm ³ /g	m ² /g	cm ³ /g	m ² /g	cm ³ /g
800°C KOH-HCl	357	363	0.085	0.23	320	0.18	690	0.78	410	0.23
800°C KOH-HCl 1000 °C	314	309	0.11	0.2	126	0.056	680	0.56	360	0.2
800°C KOH-HCl 1400 °C	222	200	0.035	0.16	74.63	0.032	480	0.41	270	0.17
450°C KOH-HCl 1400 °C							90	0.04		

CO2 SDFT vs VDFT





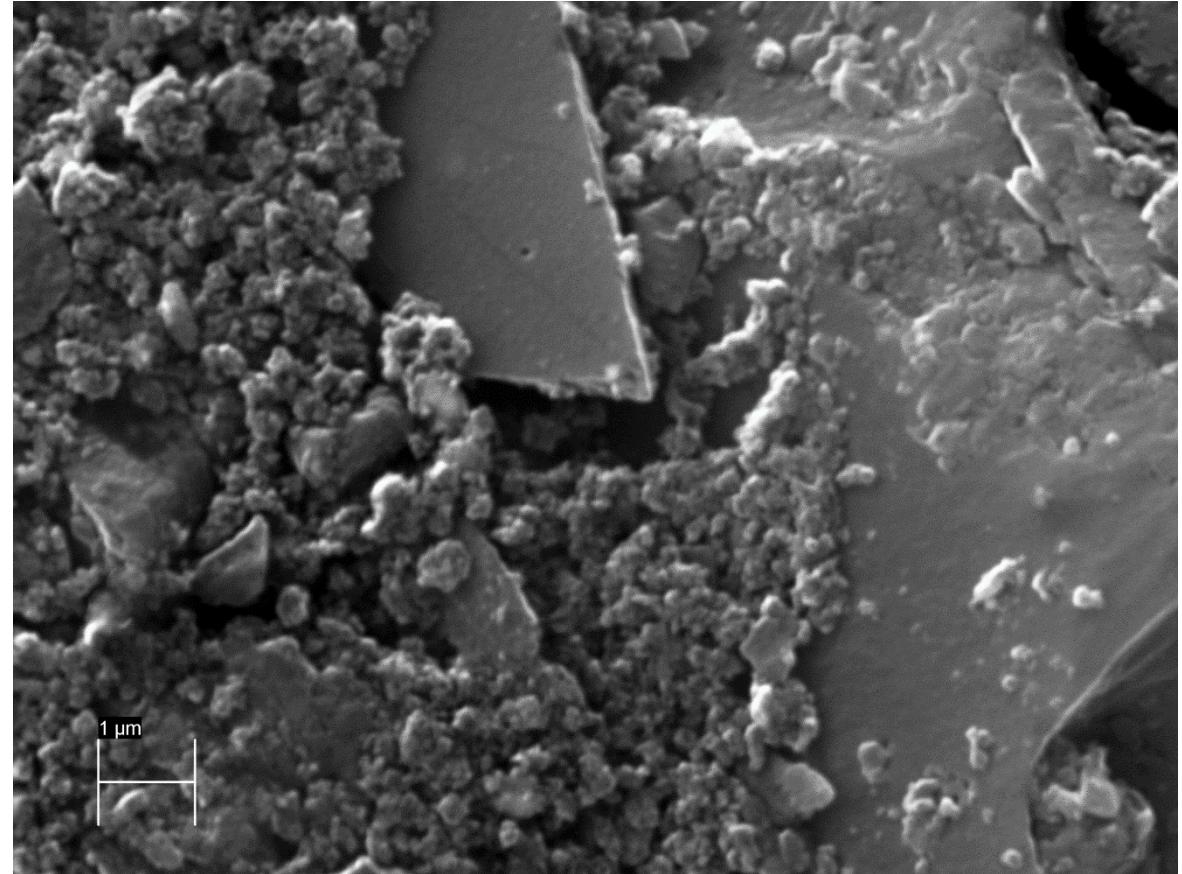
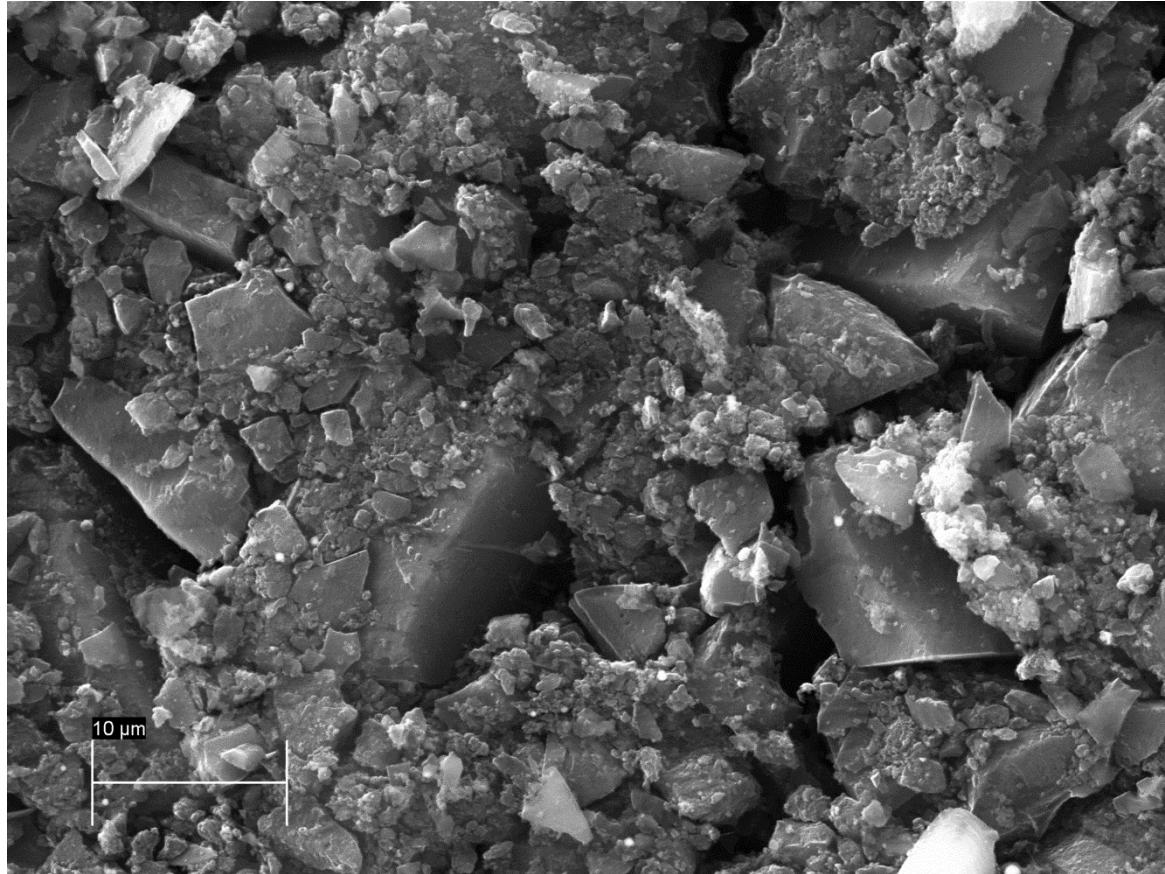
Raman spectroscopy data



Black – 600 °C
Blue – 700 °C
Green – 900 °C
Red – 1100 °C

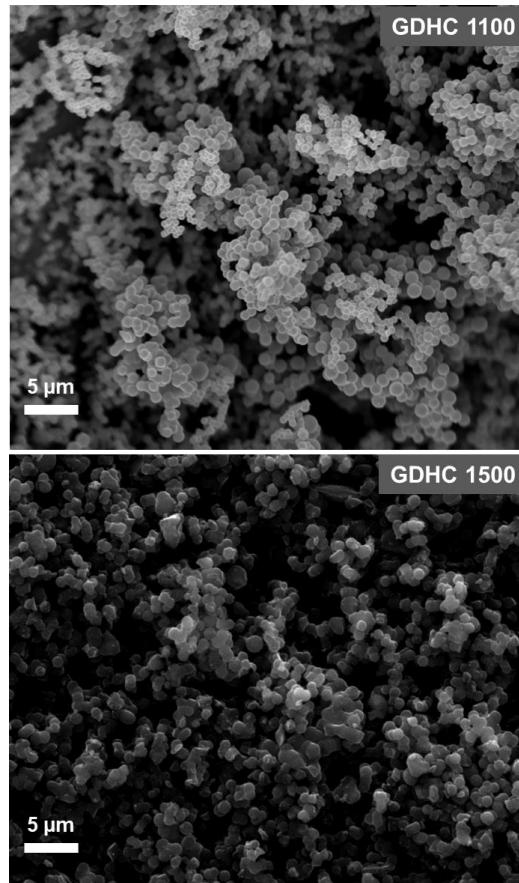
- Graphitisation process started at $T = 1173$ K!
- Materials with optimal electric conductivity can be prepared!

PDC SEM (ZnCl_2)

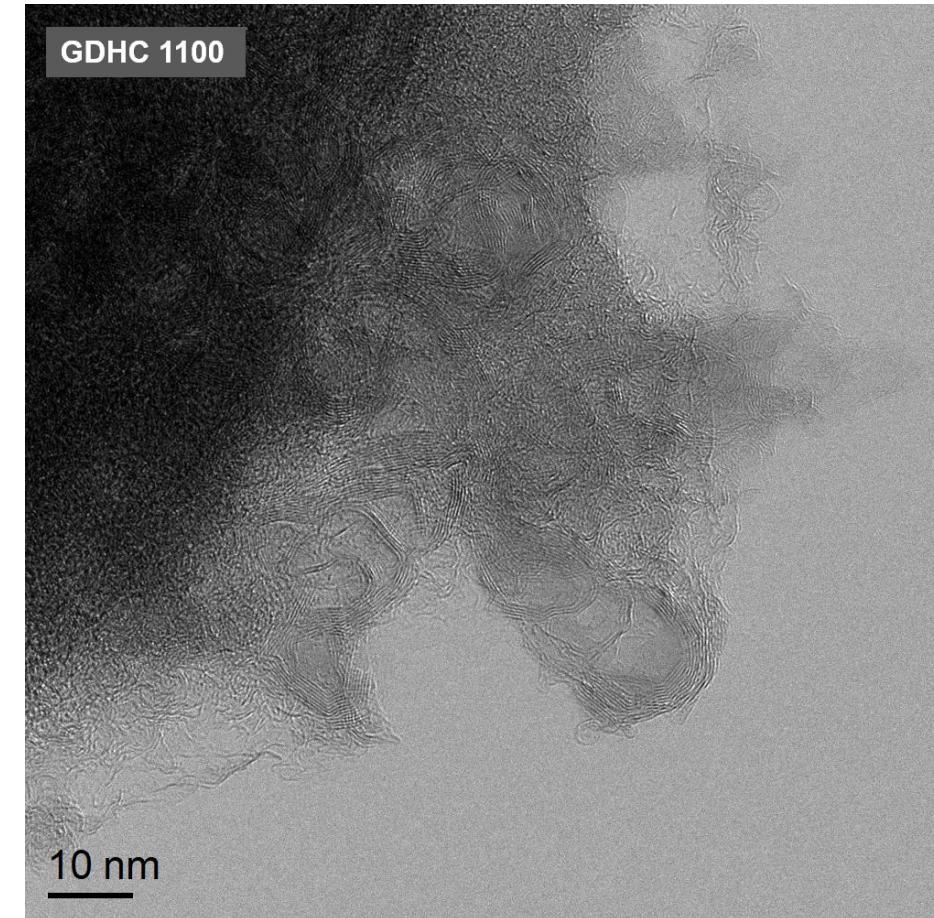


Hard sphere carbon structure

SEM



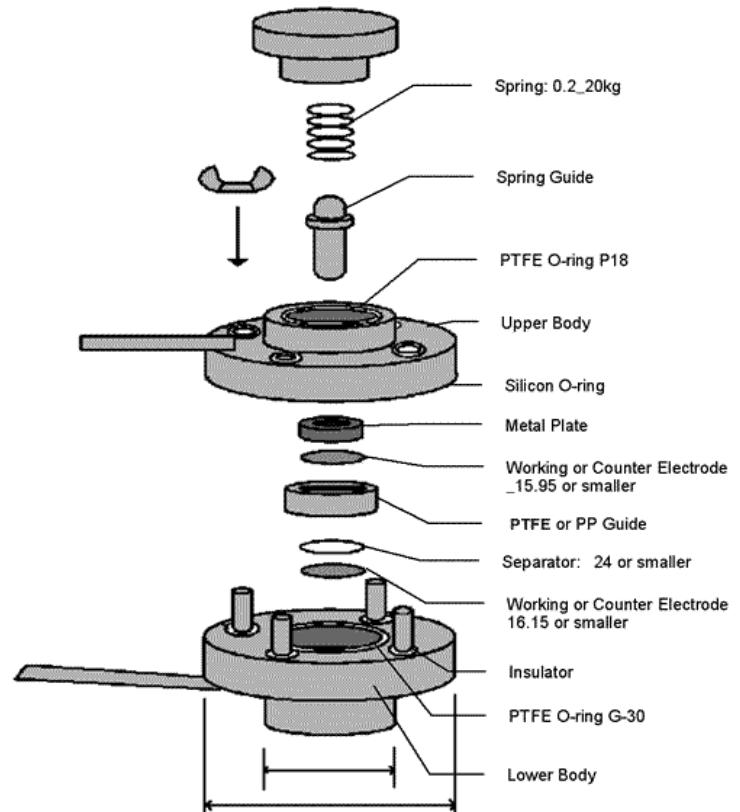
TEM

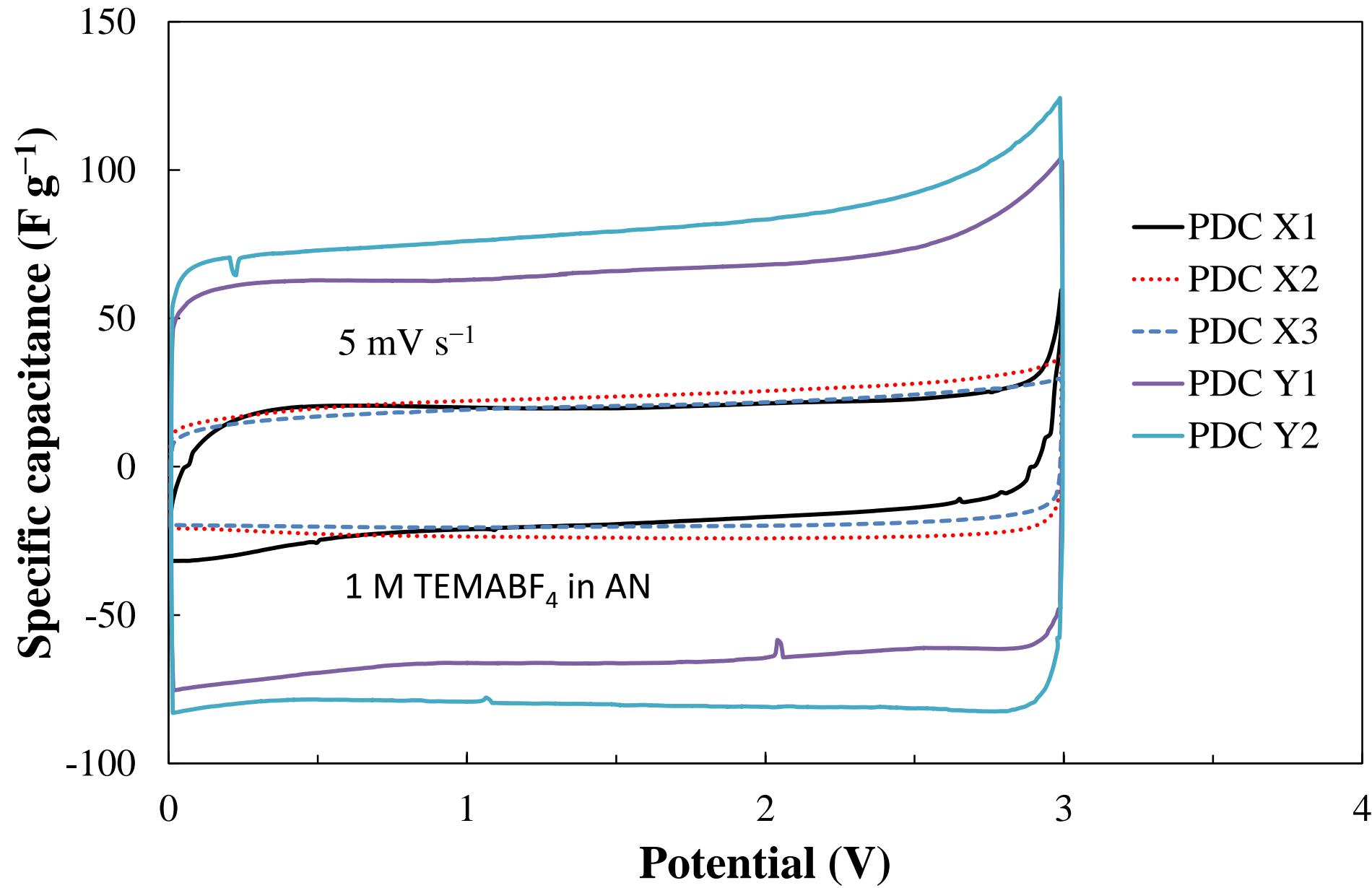


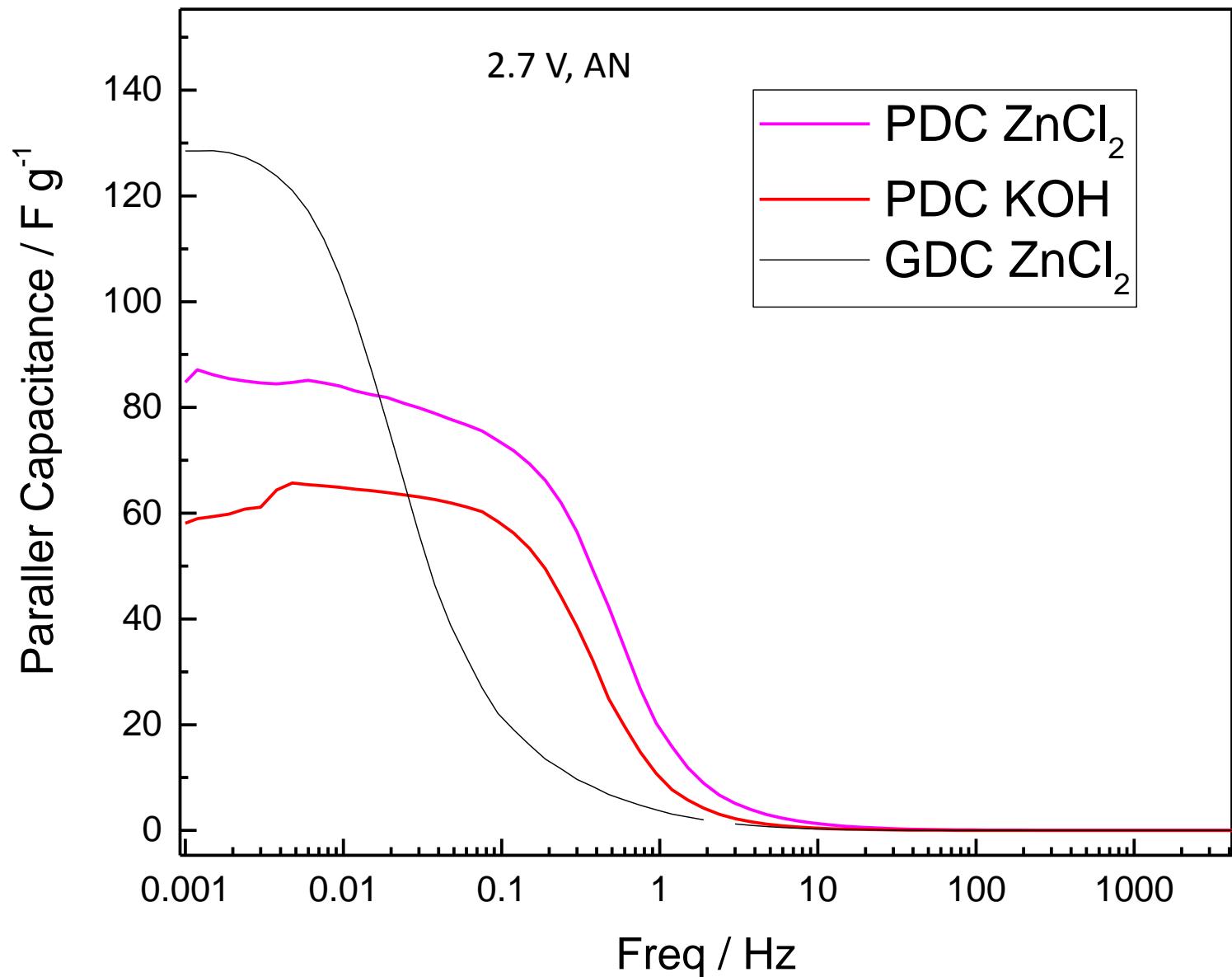
Electrochemical measurements

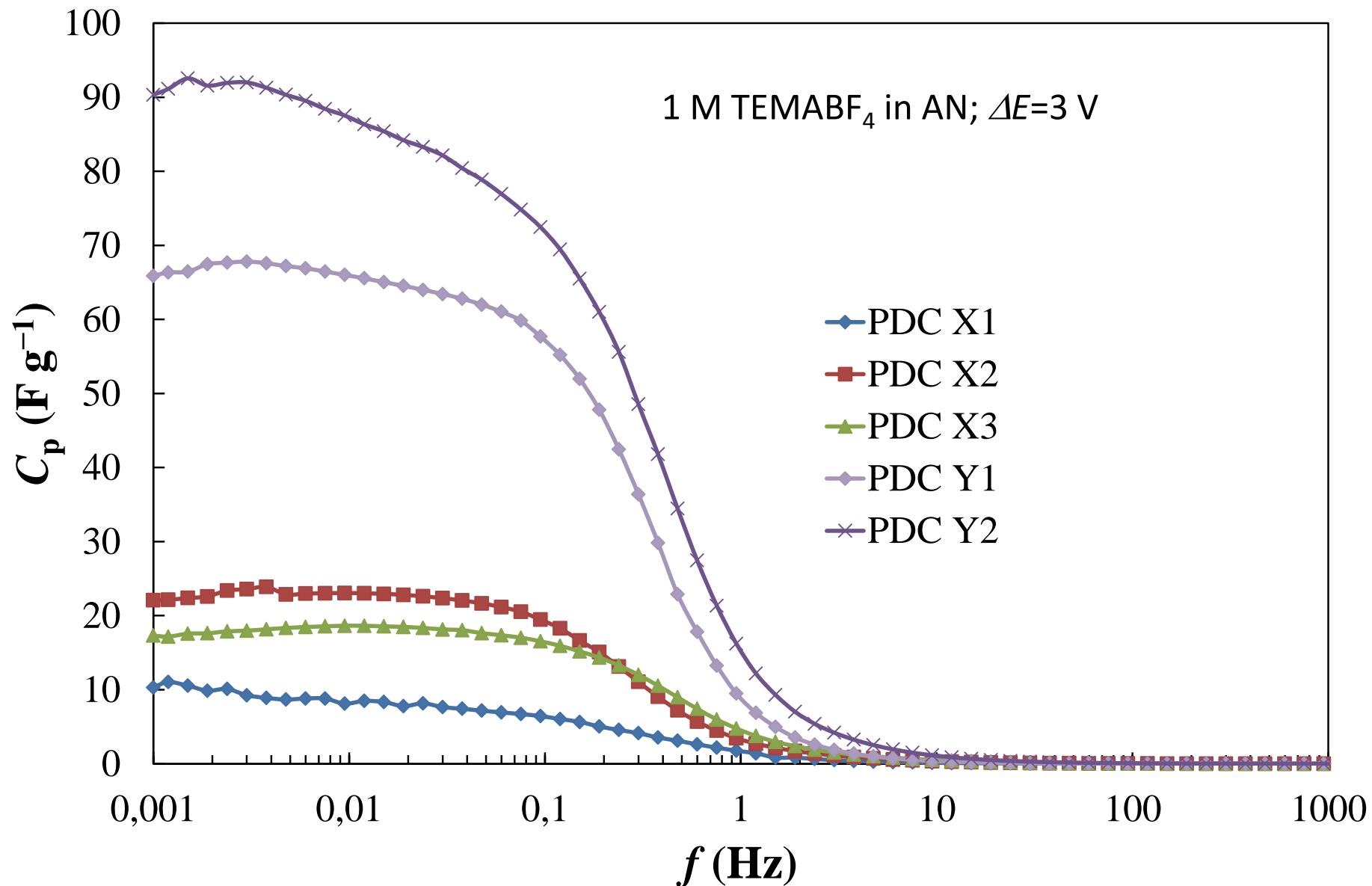
- Active material with mixture of binder (PTFE), roll-pressed, $S_{\text{electrode}} = 2 \text{ cm}^2$, thickness $L = 100 \pm 5 \mu\text{m}$
- One side covered with Al-layer (3 mm) by using plasma activated physical deposition
- Two identical peat carbon based electrodes in 1 M $(\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4$ + acetonitrile (AN)
- Glove box, O_2 and $\text{H}_2\text{O} < 0.1 \text{ ppm}$

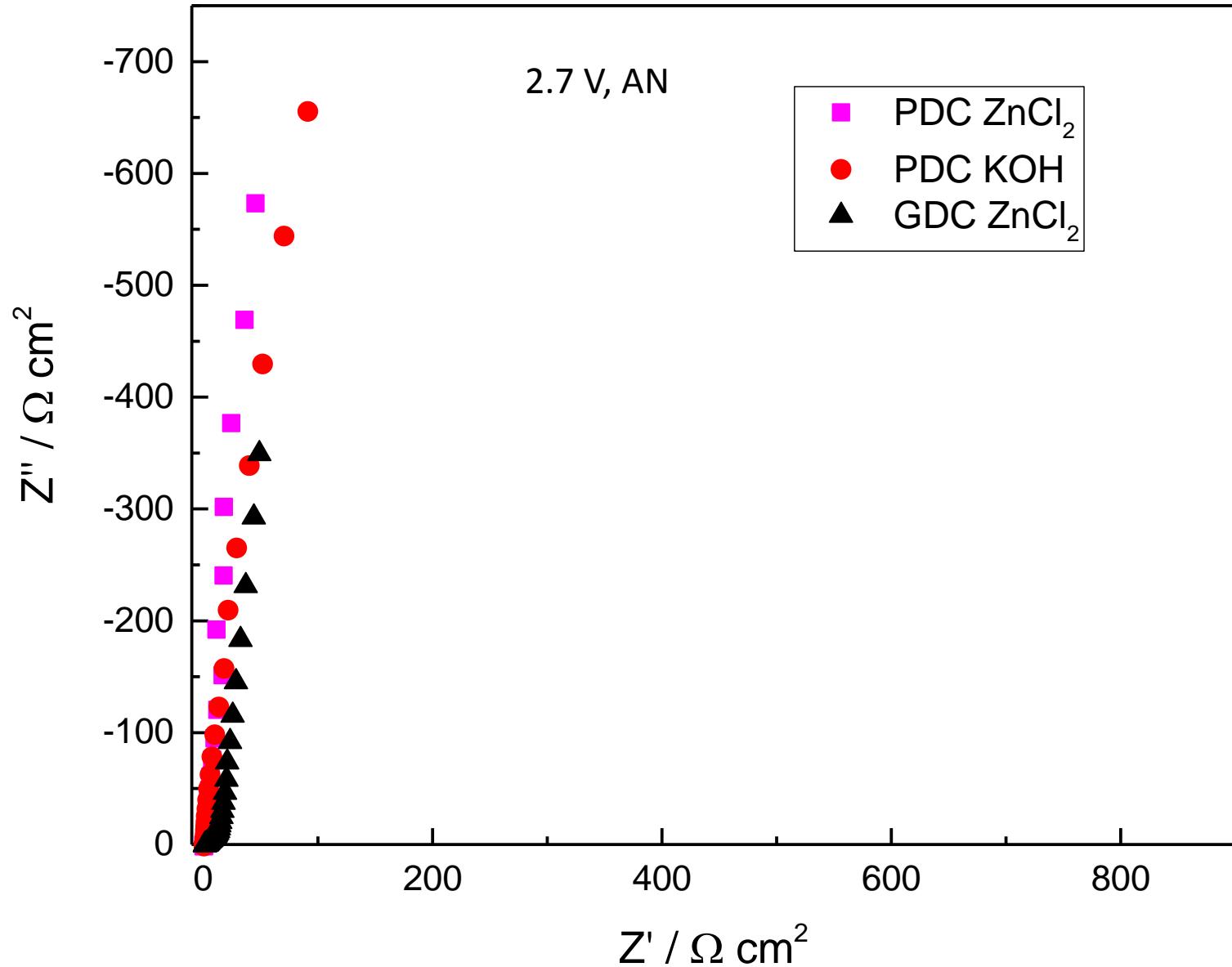
Hohsen Co test cell

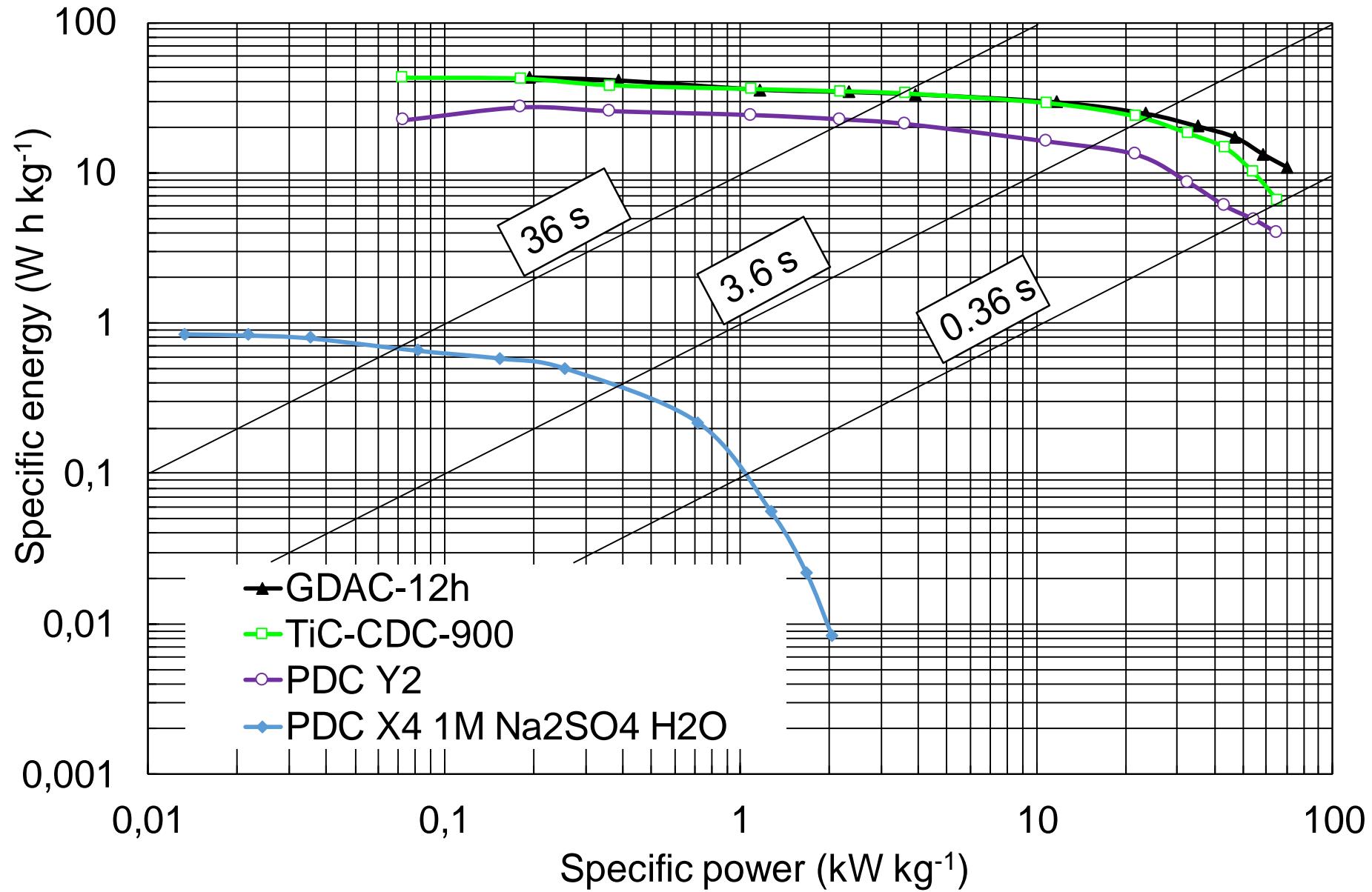




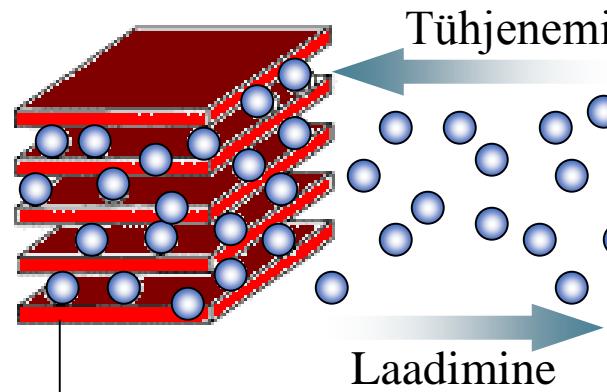






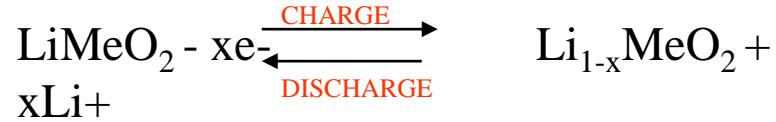


Liitium-joon ja Naatrium-joon akud

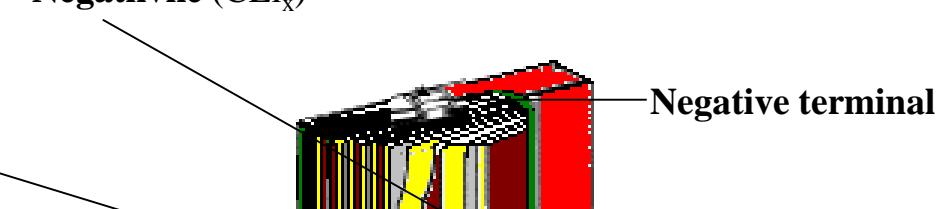
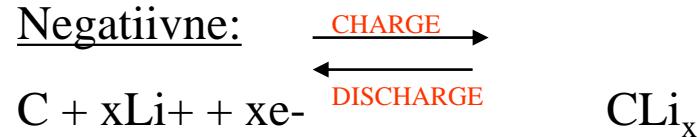


LiCoO₂-utilized for commercial batteries
LiNiO₂, LiMn₂O₄-prospective

Positiivne:



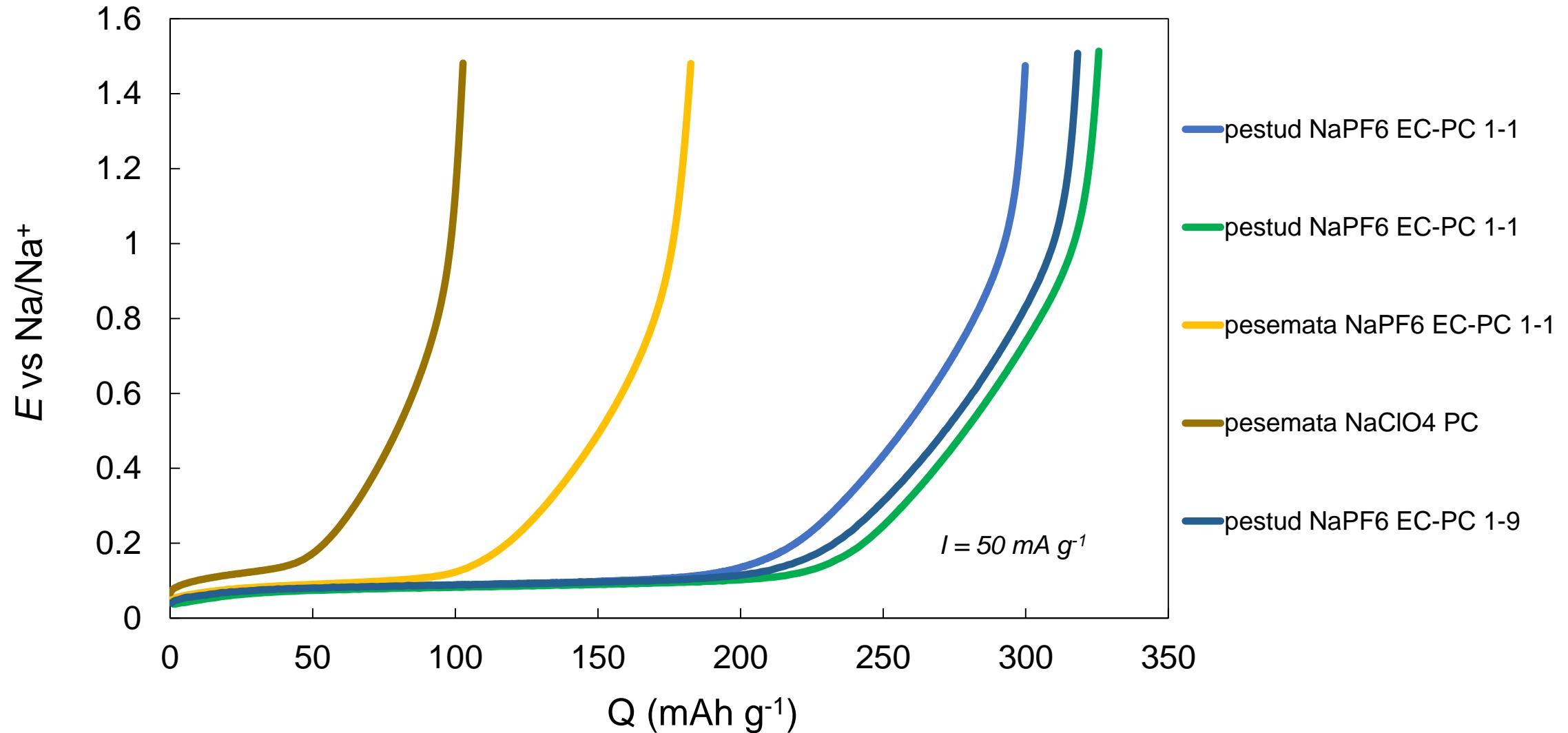
Negatiivne:

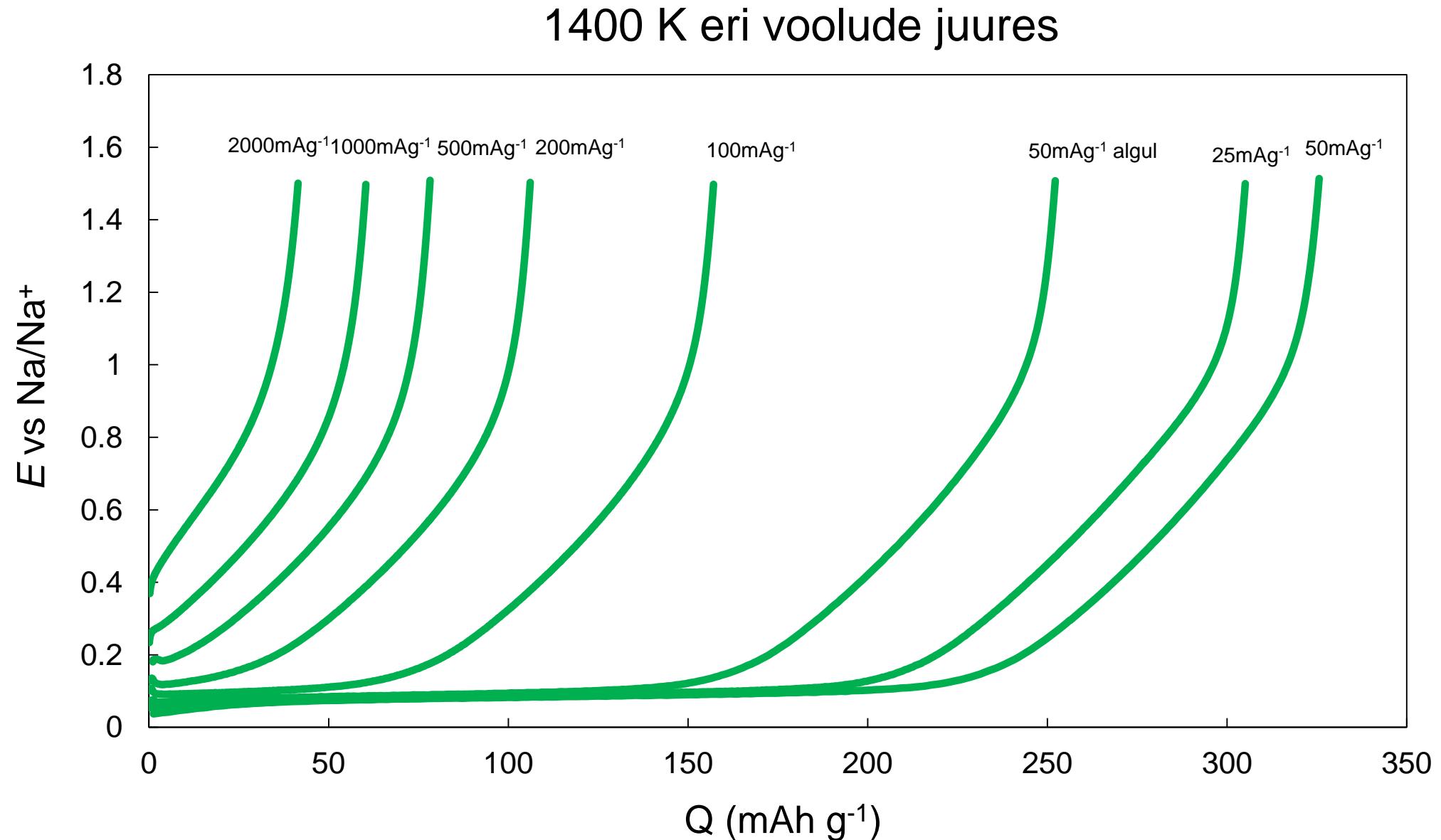


Li+ ja Na+-joon-patareid

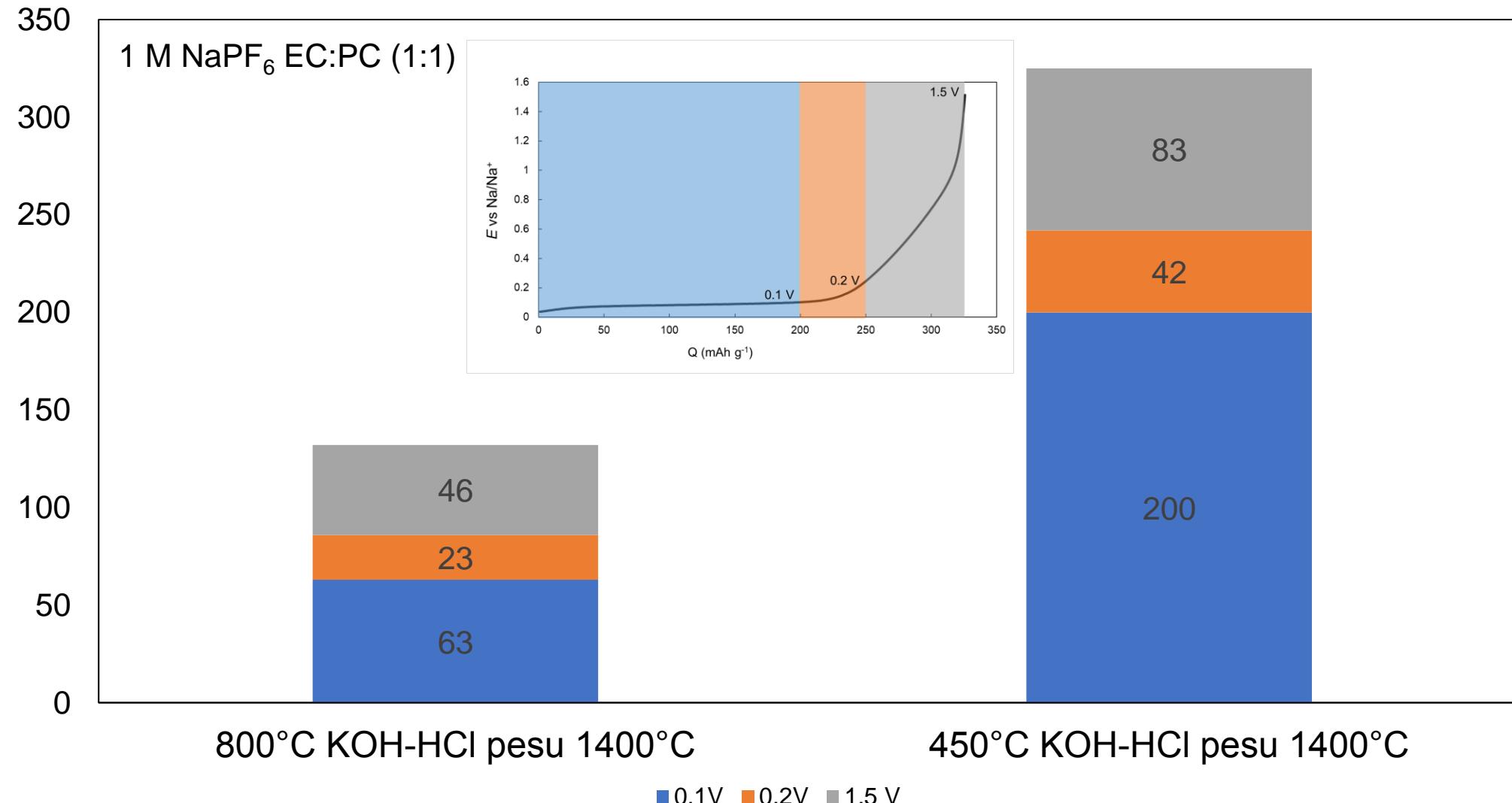
- väga palju erinevaid modifikatsioone
- limiteeriv staadium on Li+- (Na+) interkaleerumine (tungimine) või adsorbeerumine grafiidikihtide (kerade) vahele

1400 K juures sünteesitud süsinikud

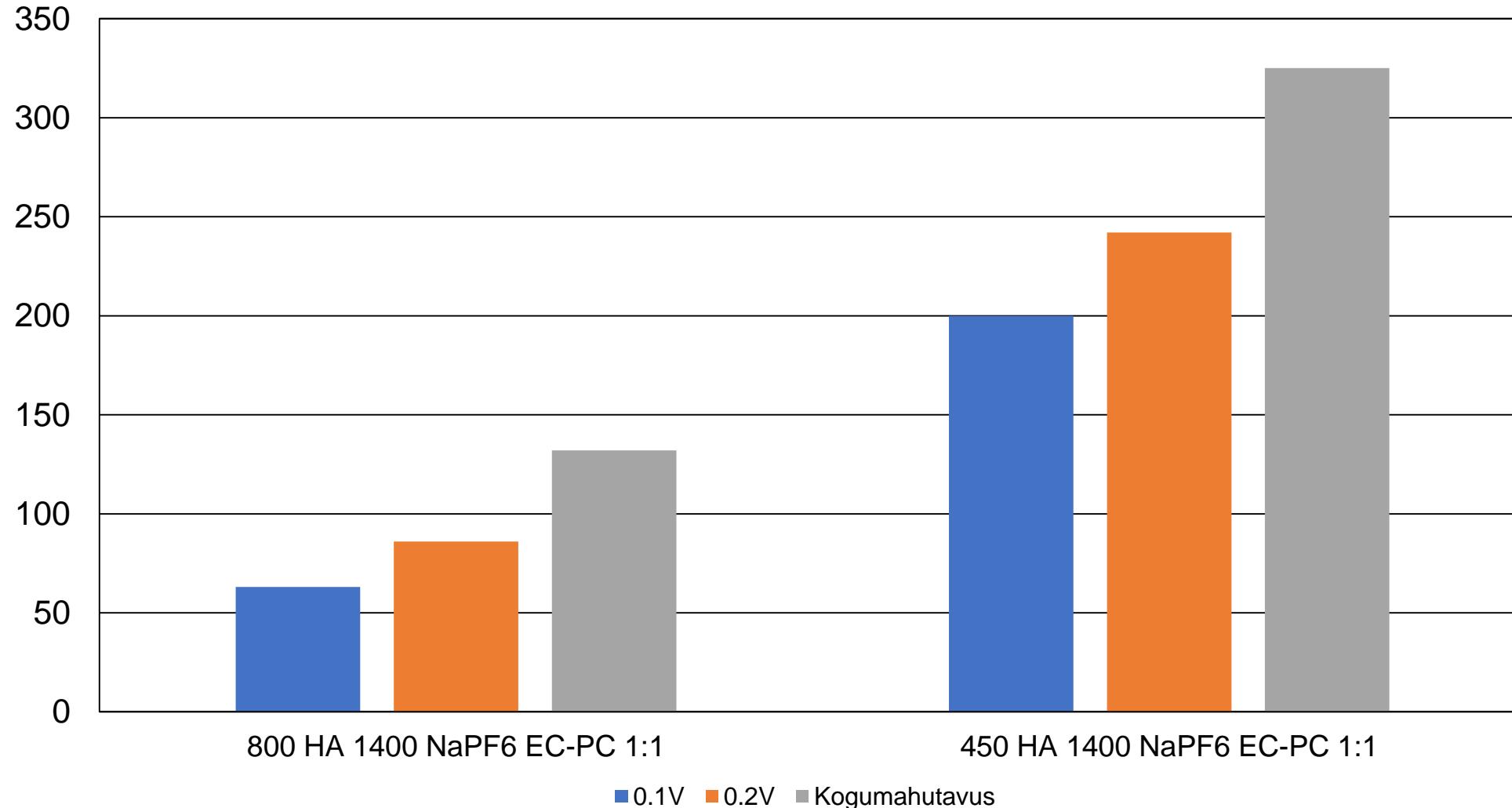




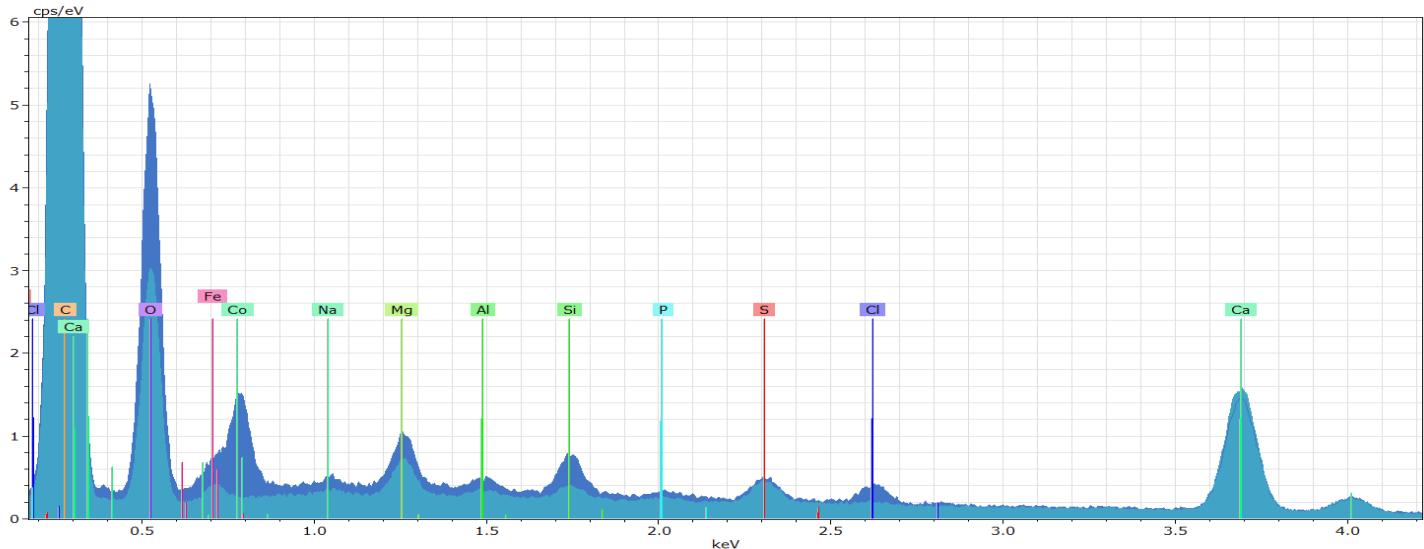
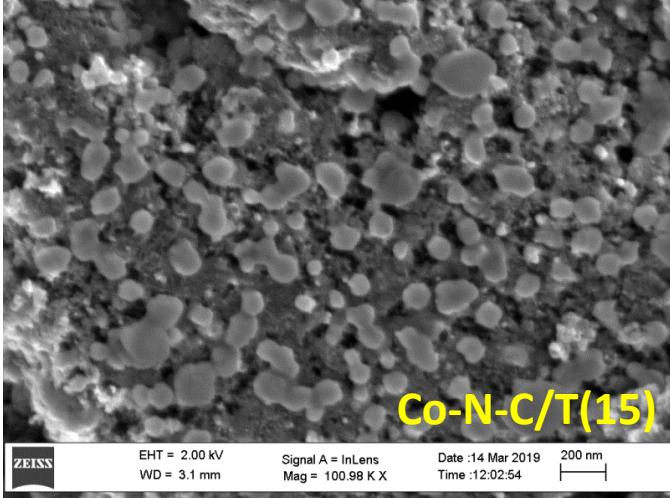
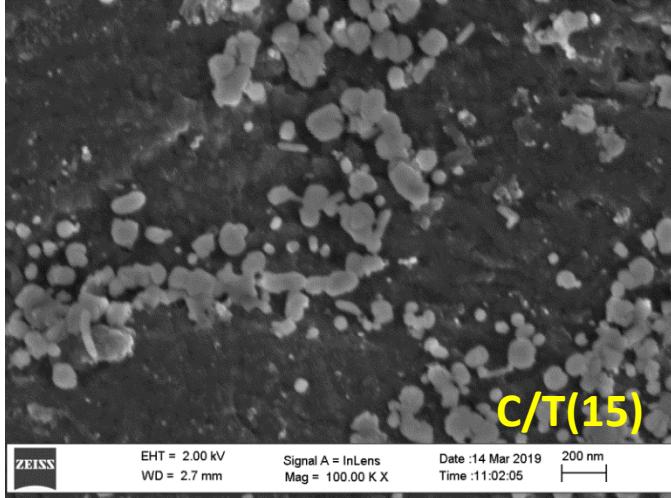
Esimese pürolüusi temperatuuri mõju



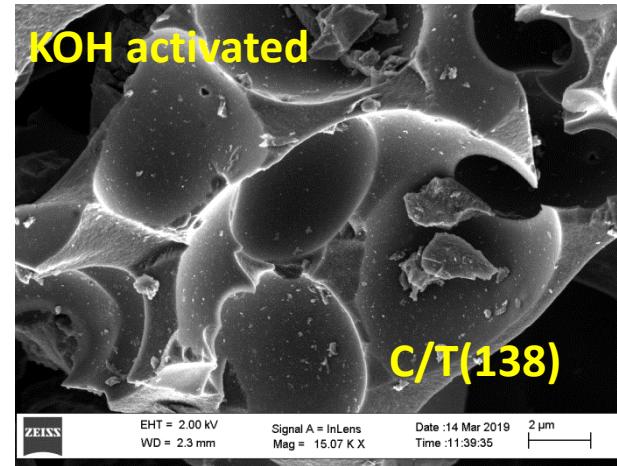
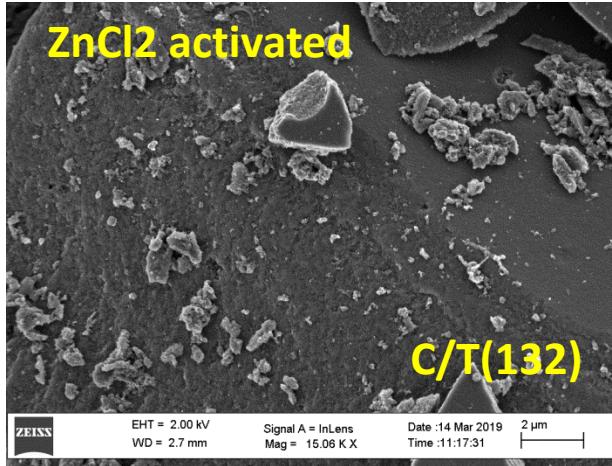
Laadimisvoolude platoode analüüs



C/T(15)- Pürolüüsitud 3h, Ar, rate 5°C /min 800oC (2 h) juures: ISI 1.1 art.: R. Jäger et al., ECS Trans. 2019,: P. Teppor, et al. *J.Electrochem Soc.*, 2019-2020. ettevalmistamine lõppjärgus.

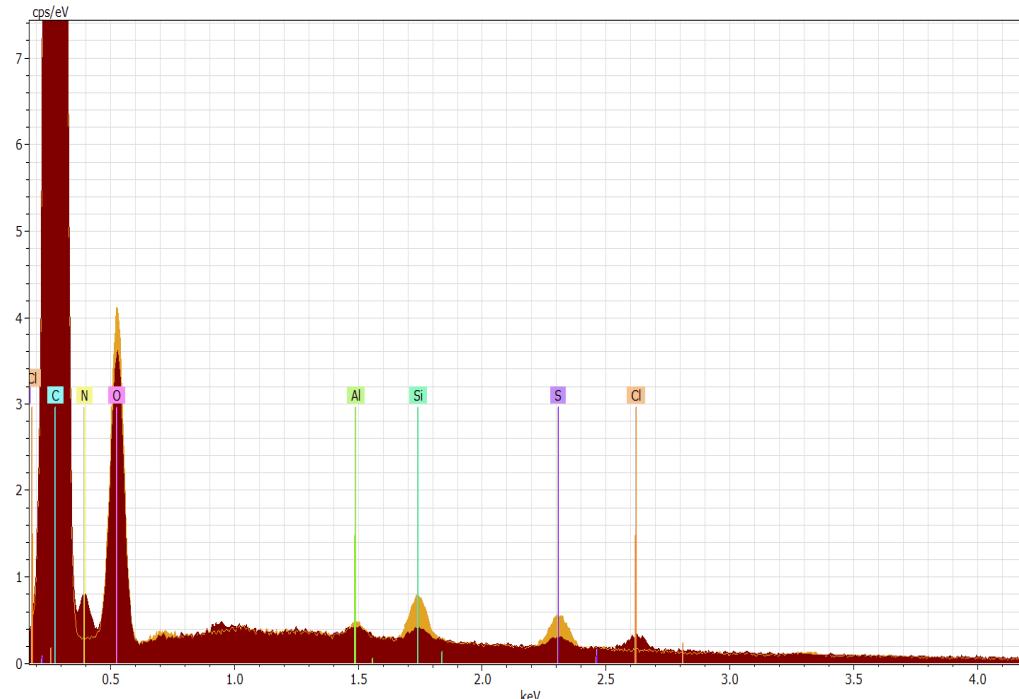


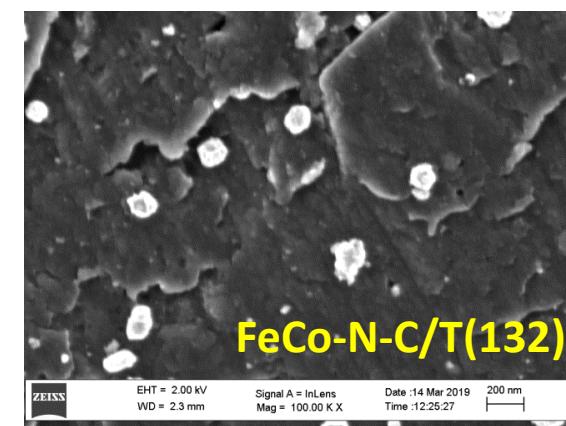
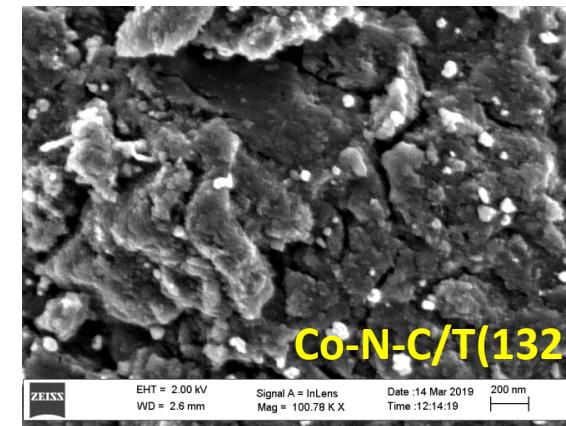
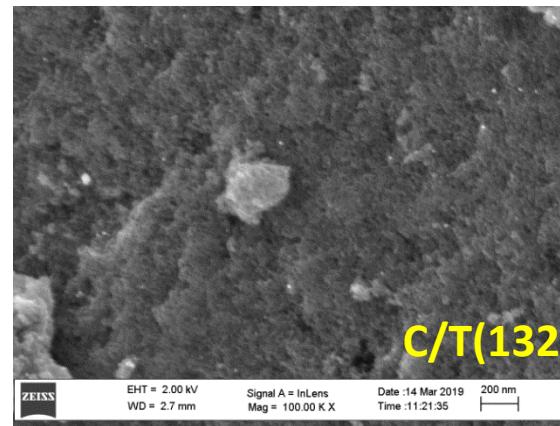
HR-SEM ja SEM-EDS



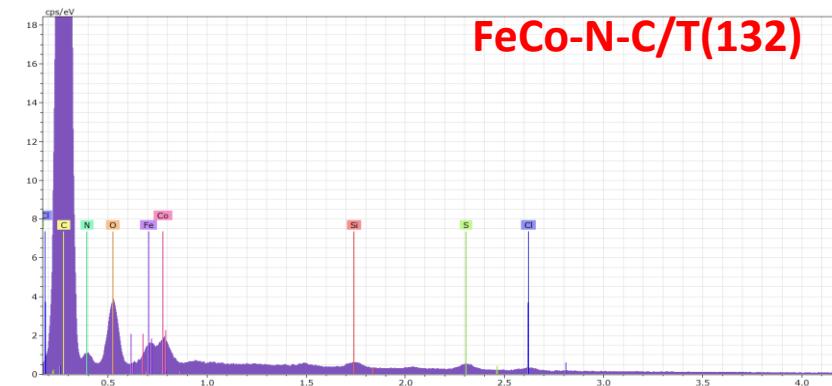
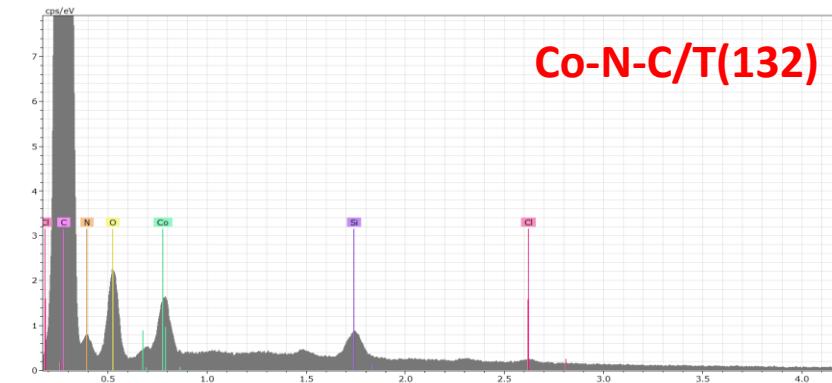
The as-received dry peat was mixed with water and blended with a blender and then left to dry in an air atmosphere. Carbon material was synthesized by activation of the hydrochar with ZnCl₂ or KOH with mass ratio 1:4 at 700°C using heating up rate of 5°C min⁻¹ (M. Härmäas)

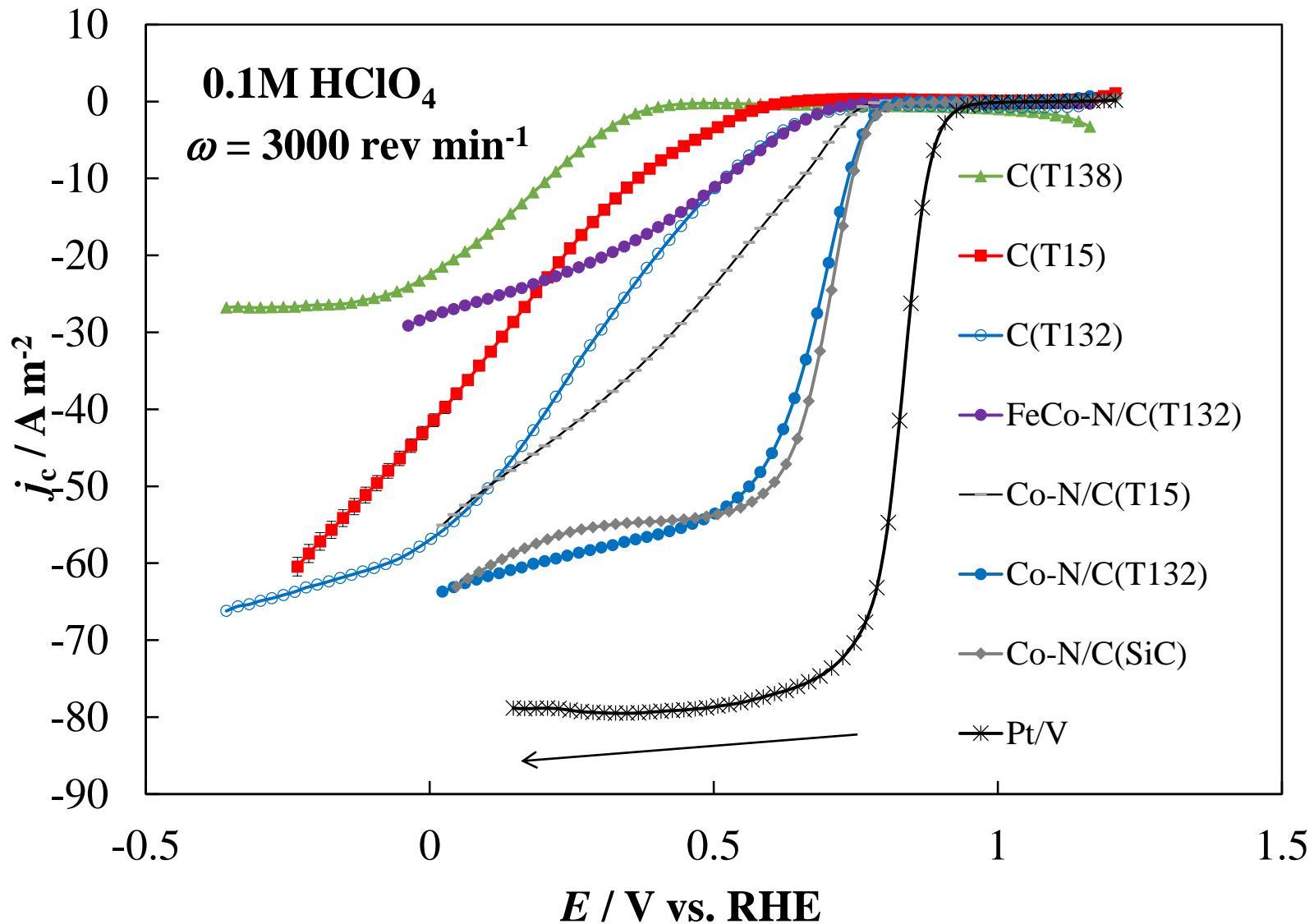
element	C(T132)	C(T138)
Süslinik	83.41	84.56
Hapnik	9.80	11.10
Lämmastik	5.68	2.49
Kloor	0.43	-
Räni	0.30	0.97
Väävel	0.25	0.75
Alumiinium	0.14	0.14





element	C(T132)	Co-N-C(T138)	FeCo-N-C(T138)
Süsik	83.41	83.92	81.02
Hapnik	9.80	6.19	7.19
Lämmastik	5.68	5.75	5.43
Koobalt	-	2.97	2.20
Raud	-	-	3.08
Kloor	0.43	0.15	0.28
Räni	0.30	1.02	0.35
Väävel	0.25	-	0.44
Alumiinium	0.14	-	-





RDE



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Turbast toodetud eriotstarbeliselt aktuveeritud süsinik sobib elektrokeemilistesse süsteemidesse, kuid valjalikud on väga süstemaatilised täiendavad peenuuringud!

Publikatsioon: M.Härmas, R.Palm, T.Thomberg, R.Härmas, M.Koppel, M.Paalo, I.Tallo, T.Romann, A.Jänes, E.Lust:

Hydrothermal and peat - derived carbons as electrode materials for high - efficient electrical double-layer capacitors: J.of Applied Electrochem.
<https://doi.org/10.1007/s10800-019-01364-5d>

Tänan tähelepanu eest!