pragolab

Analytické přístupy k alternativním zdrojům energie

Jaroslav Novák

Alternativní zdroje energie

- Slunce

- Vítr

- Termální prameny

- Tepelná čerpadla
- Vodní elektrárny

- VODÍK

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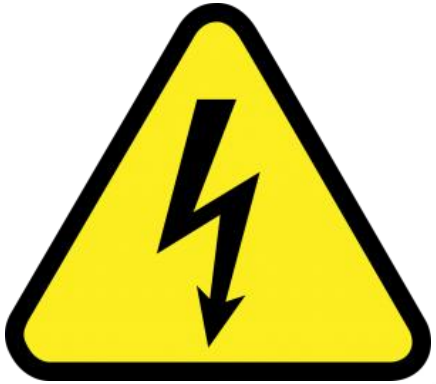


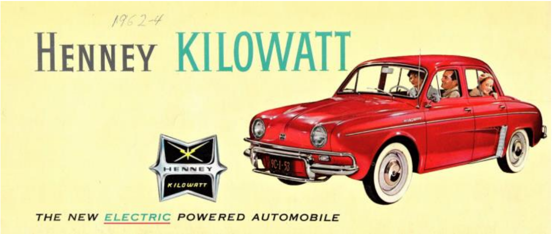
elektrická energie

využití

- Osvětlení
- Vytápění
- Přístroje
- **Pohon aut**

Elektromobilita a BATERIE

- **Elektromotor** - 1828 kněz Štefan Anián Jedlík
- **Elektromobil** – 1835 Stratingh a Becker, 1895 František Křižík
- Na přelomu 19. a 20. století více elektromobilů než aut se spalovacím motorem



- Mnoho typů **baterií**
- Nejrozšířenější Lithium-iontová baterie (Li-Ion) – 90% jednorázových, 95% dobíjecích

- **Kritické parametry**:

Kapacita, životnost, bezpečnost

Výroba, recyklace

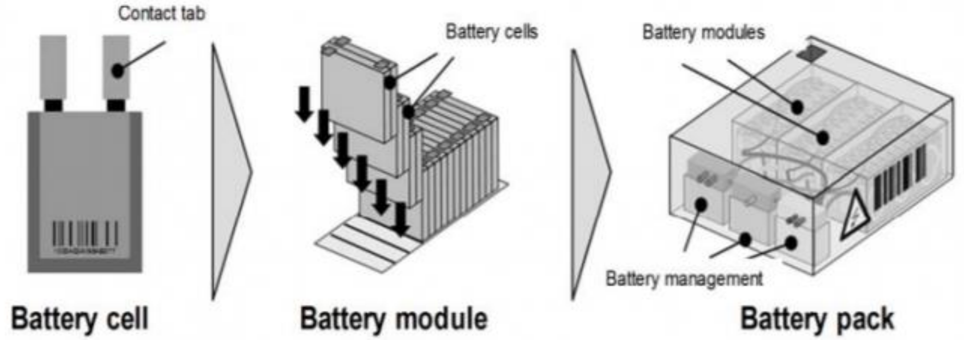
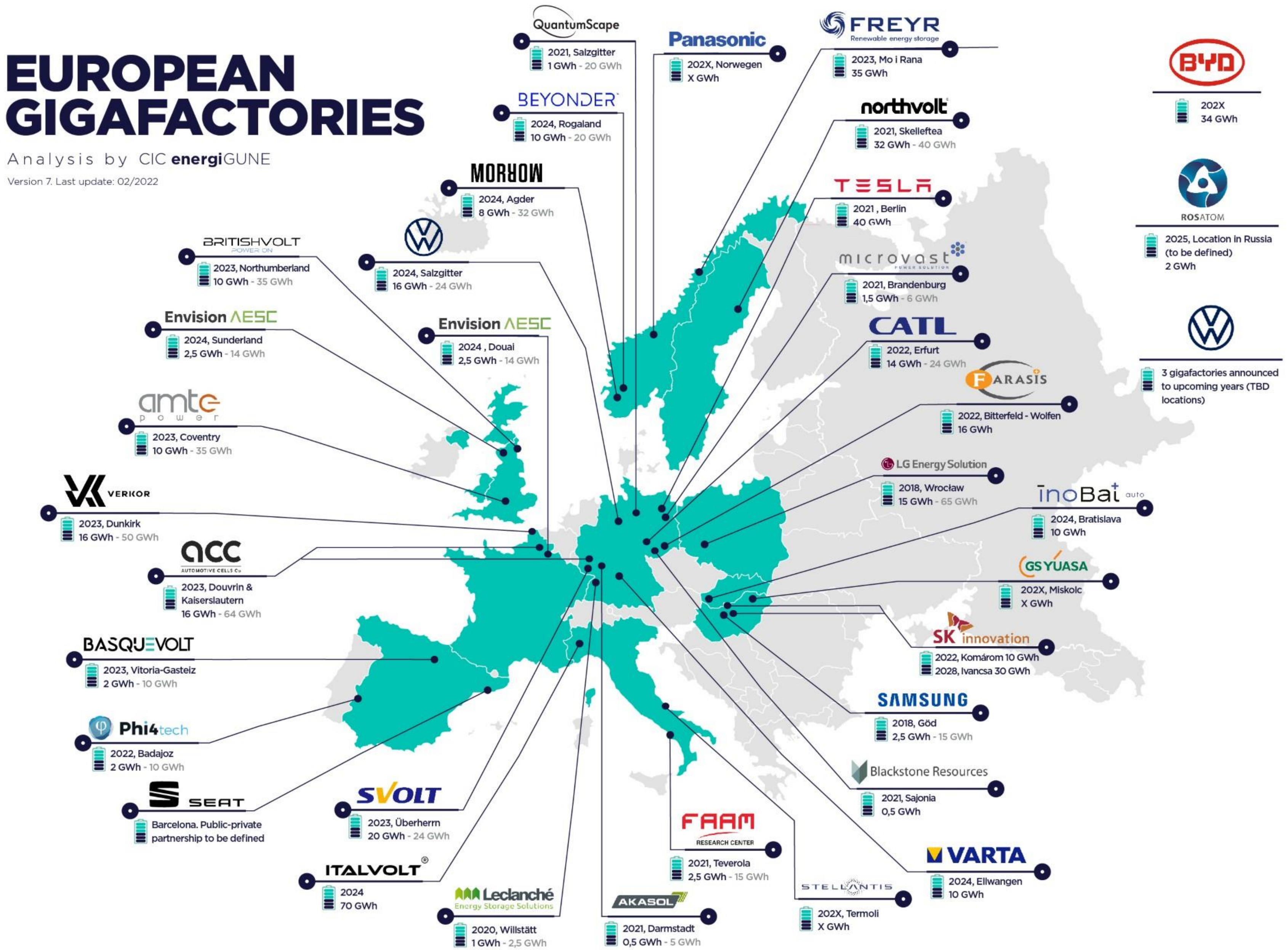
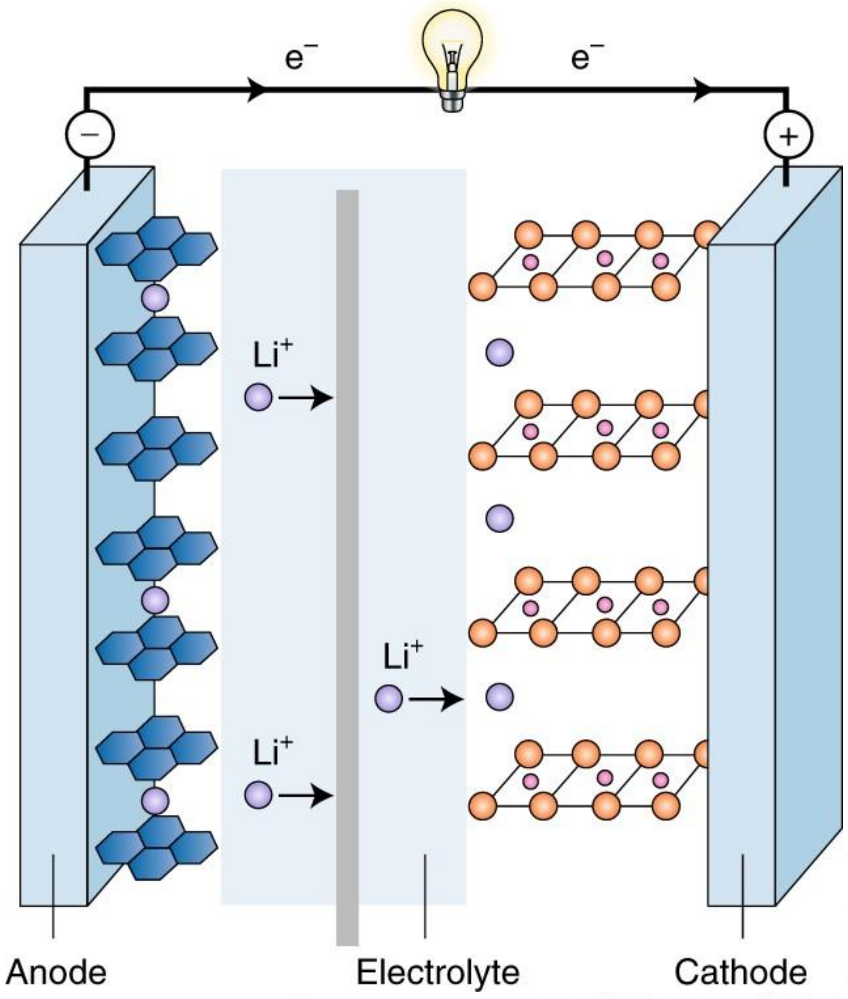


Fig. 1 From battery cells to a battery pack

Baterie pro elektromobily

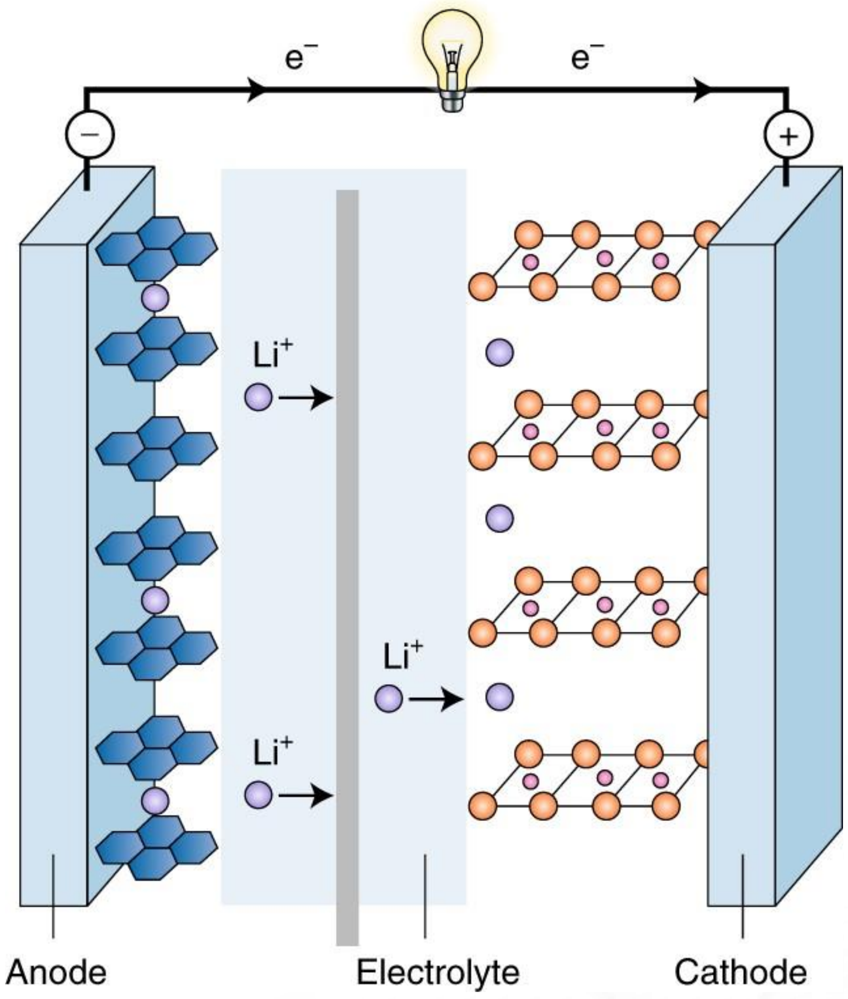


Li-Ion baterie



- **Anoda** - obvykle z uhlíku (grafit) – LiC_6, $LiC_6 \rightarrow C_6 + Li^+ + e^-$
- **Katoda** - oxid lithiového kovu ($LiCoO_2$, $LiFePO_4$ nebo $LiMn_2O_4$)
- **Elektrolyt** = organická rozpouštědla + vodivá lithiová sůl ($LiPF_6$), aditiva
- Propustný membránový **separátor** – umožňuje pohyb Li^+ mezi anodou a katodou, zabraňuje zkratu
- **Kvantifikace** výkonu baterie (anoda, katoda a elektrolyt) vyžaduje řadu analytických technologií
- Přístroje **Thermo Scientific** pokrývají všechny analytické aspekty Li-ion baterií

Ztráta životnosti baterie



- **Anoda** – růst SEI (rozhraní pevného elektrolytu) – SEI nezbytné pro fungování, ale snižuje proud a nabíjecí kapacitu
- **Katoda** - růst SEI způsobené oxidací elektrolytu
  - redukce oxidu lithiového kovu
- **Elektrolyt** – jeho rozklad za vzniku plynných i netěkavých látek
  - ztráta cyklovatelného Li

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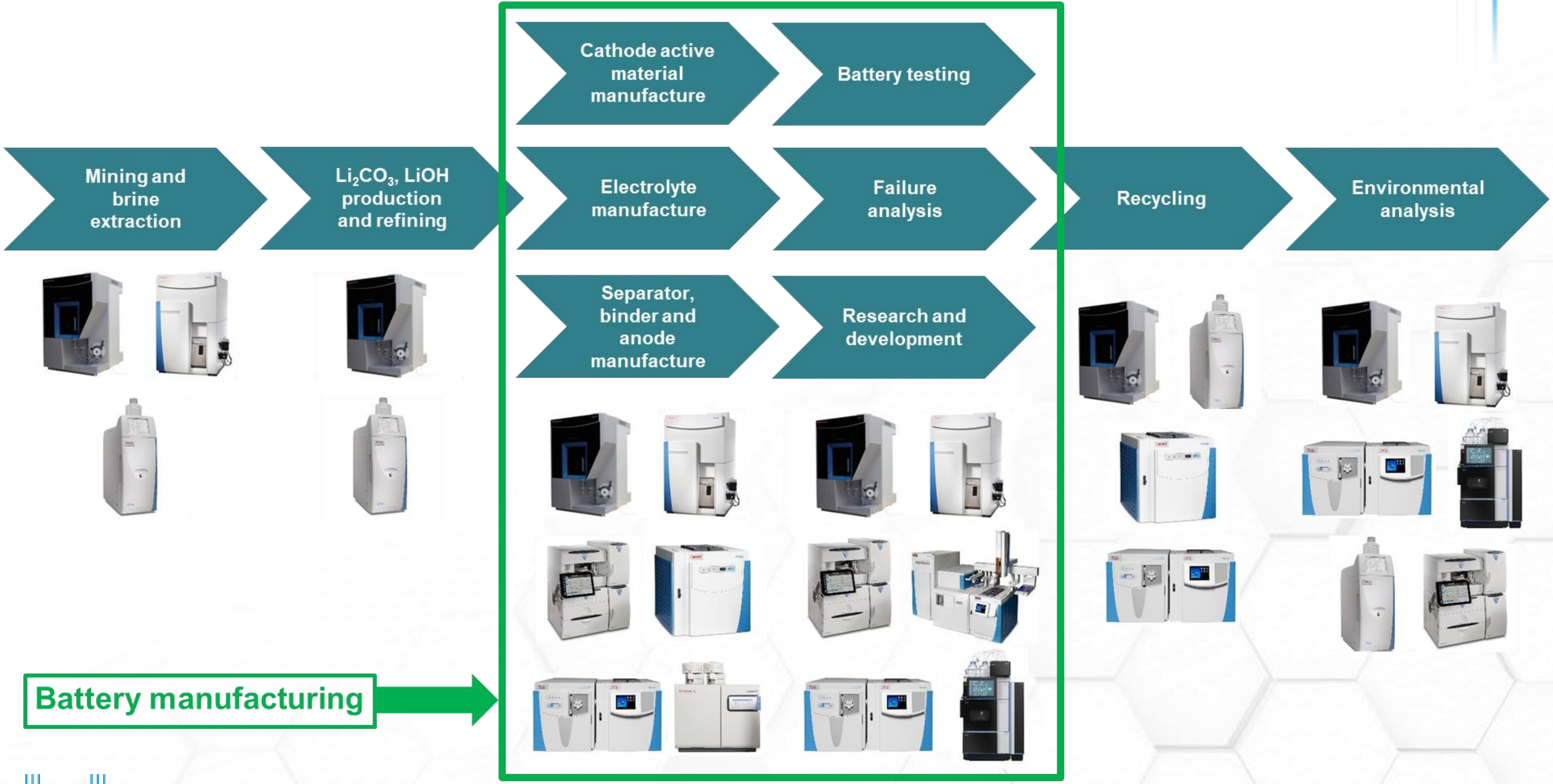
Baterie – výrobní postup a místa pro analytiky

- Čistota surovin
- Vlastní výroba
- Vývoj
- Recyklace



- Anoda
- Katoda
- Elektrolyt

Li-Ion baterie – analýza složení elektrolytu

Application update | 002026

Thermo Fisher SCIENTIFIC

Battery solutions

Determination of tetrafluoroborate, perchlorate, and hexafluorophosphate in an electrolyte sample for lithium-ion battery production

Author
Hua Yang, Jeffrey Rohrer, Thermo Fisher Scientific, Sunnyvale, CA, US

Keywords
Dionex IonPac AS20 column, suppressed conductivity detection, RFIC

Goal

To update the application that determined tetrafluoroborate, perchlorate, and hexafluorophosphate in an electrolyte sample that was designed to simulate a lithium-ion battery production sample with new equipment and a current generation electrolytic suppressor

Introduction

Rechargeable batteries are an increasing part of our daily life as we use more portable electronic devices, including mobile phones. These batteries are also important for the electric car industry. Lithium-ion batteries are the most commonly used rechargeable batteries because of their high volumetric energy density.[1] The electrolyte in these batteries are lithium salts in non-aqueous solutions. Commonly used lithium salts are lithium hexafluorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium hexafluorosilicate ($LiSiF_6$), and lithium tetraphenylborate ($LiB(C_6H_5)_4$). Commonly used organic solvents are ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, methyl formate, methyl acrylate, methyl butylate, and ethyl acetate.[1] The electrolyte in lithium batteries may have a mixture of these lithium salts and organic solvents. The electrolyte's concentration in the solvent ranges from 0.1 to 2 M, with an optimal range of 0.8 to 1.2 M. The anions of the added lithium salts can be determined by ion chromatography (IC) to ensure that the solutions have been prepared at the proper

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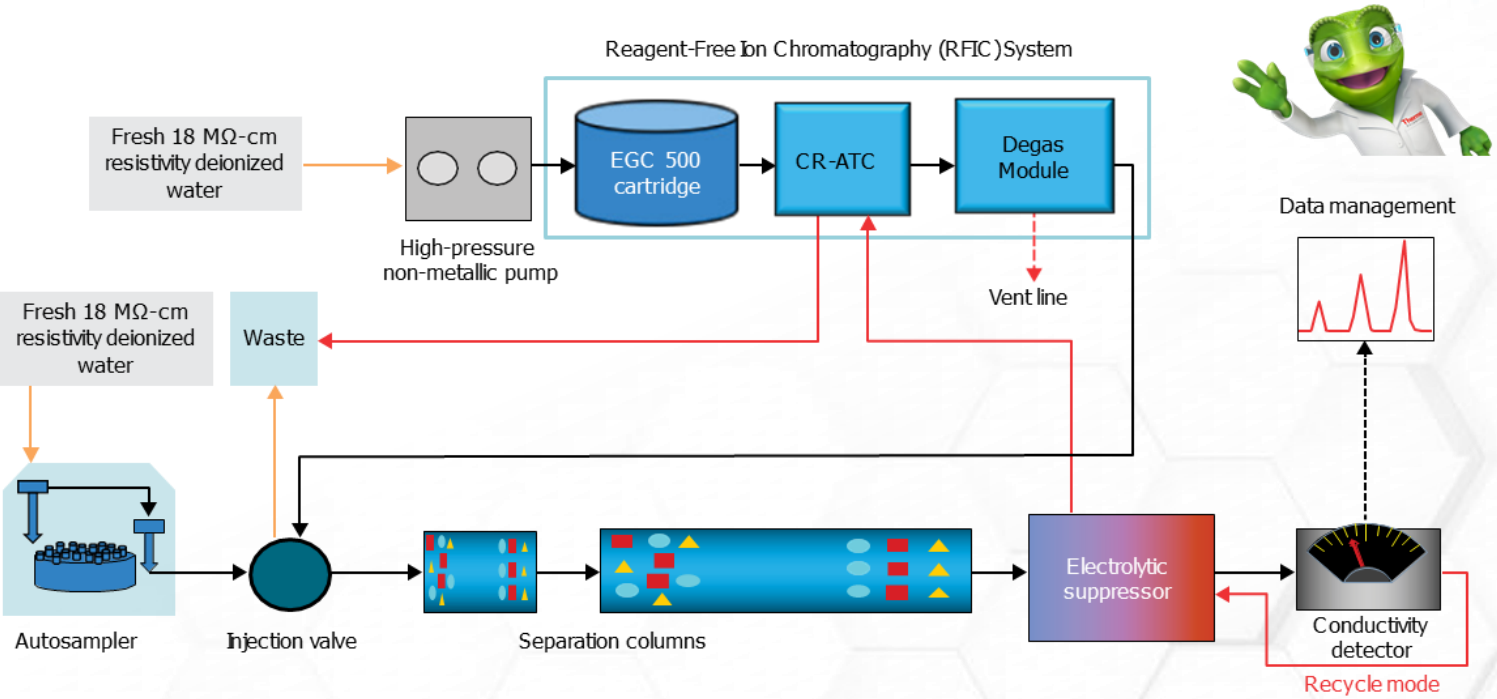
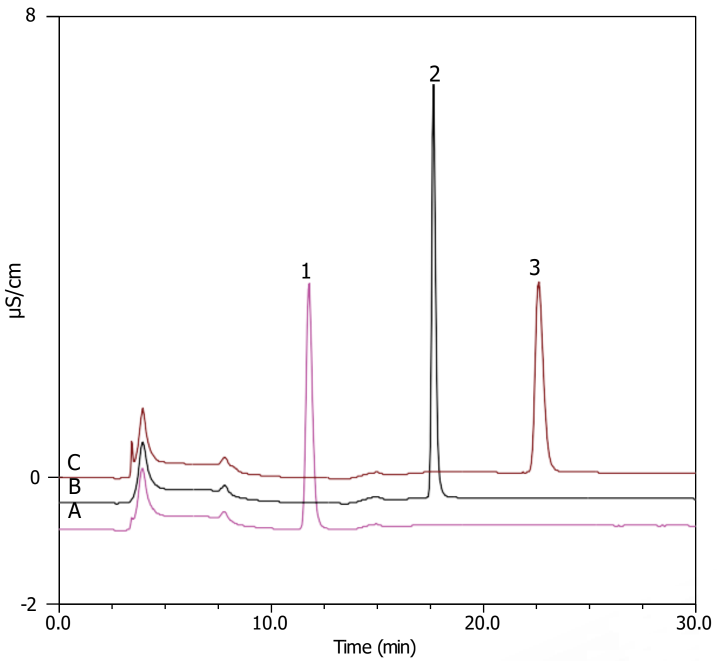


Li-Ion baterie – analýza složení elektrolytu

- **Vzorky byly pouze naředěny 1:10 000 a 1:5 000**



Columns: Dionex IonPac AG20, 2 × 50 mm and Dionex IonPac AS20, 2 × 250 mm
Eluent: Potassium hydroxide (KOH) gradient
Gradient: 0–15 min, 15 mM; 10–13 min, 80 mM; 13–26 min, 80 mM; 26–30 min, 15 mM
Eluent source: Dionex EGC KOH cartridge with Dionex CR-ATC and Dionex high pressure degasser
Flow rate: 0.30 mL/min
Inj. volume: 10 µL (Full loop)
Column temp.: 30°C
Sampler temp.: 4°C
Detection: Suppressed conductivity, Dionex ADRS 600 suppressor, 2 mm, 30°C, 70 mA, recycle mode

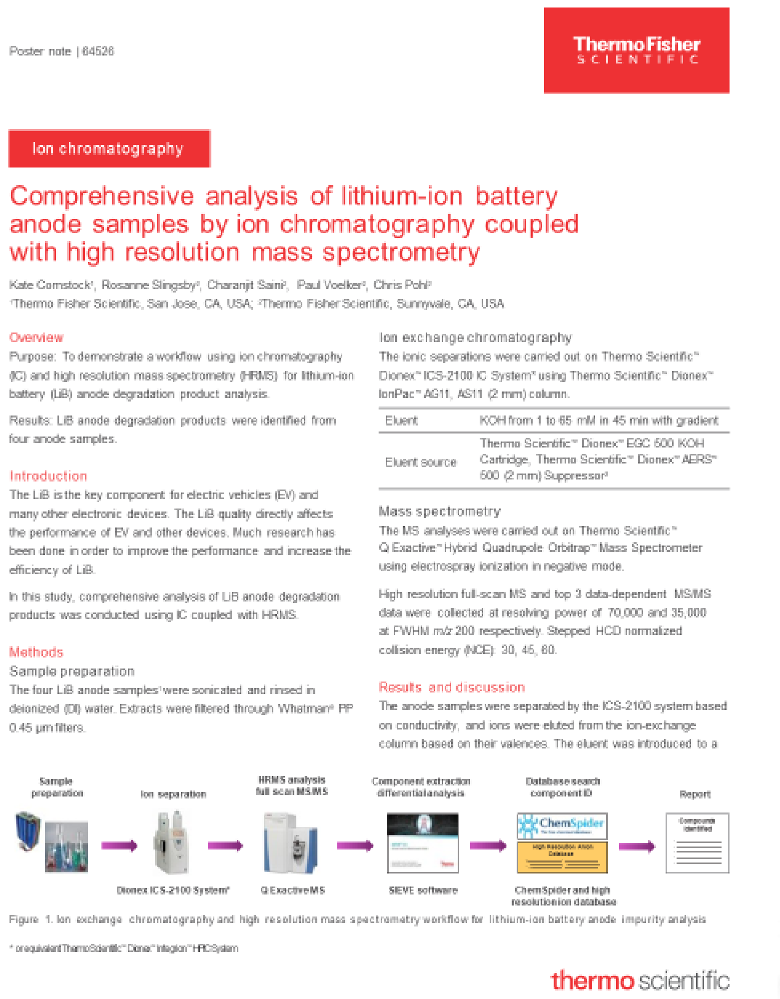
Samples: A – 10000× of 1 M Lithium Tetrafluoroborate* B – 10000× of 1 M Lithium Perchlorate* C – 5000× of 0.5 M Lithium Hexafluorophosphate**

*In 1:1:1 mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate.
** In 1:1 DI water /mixed carbonate solvents

Peaks: min
1-Tetrafluoroborate 11.8
2-Perchlorate 17.5
3-Hexafluorophosphate 22.6

Analyte	Calculated concentration (mg/L)	Average measured concentration (mg/L)	Recovery (%)	Spiked concentration (mg/L)	Average measured concentration (mg/L)	Recovery (%)
Tetrafluoroborate	8.70	9.72	112	2	11.7	109
Perchlorate	9.95	9.32	94	2	11.3	94
Hexafluorophosphate	14.5	14.7	101	2	16.9	102

Li-Ion baterie – degradace elektrolytu – identifikace sloučenin



Poster note | 64526

Thermo Fisher SCIENTIFIC

Ion chromatography

Comprehensive analysis of lithium-ion battery anode samples by ion chromatography coupled with high resolution mass spectrometry

Kate Comstock[1], Rosanne Slingsby[2], Charanjit Saini[2], Paul Voelker[2], Chris Pohl[2]
[1]Thermo Fisher Scientific, San Jose, CA, USA; [2]Thermo Fisher Scientific, Sunnyvale, CA, USA

Overview

Purpose: To demonstrate a workflow using ion chromatography (IC) and high resolution mass spectrometry (HRMS) for lithium-ion battery (LiB) anode degradation product analysis.

Results: LiB anode degradation products were identified from four anode samples.

Introduction

The LiB is the key component for electric vehicles (EV) and many other electronic devices. The LiB quality directly affects the performance of EV and other devices. Much research has been done in order to improve the performance and increase the efficiency of LiB.

In this study, comprehensive analysis of LiB anode degradation products was conducted using IC coupled with HRMS.

Methods

Sample preparation

The four LiB anode samples[1] were sonicated and rinsed in deionized (DI) water. Extracts were filtered through Whatman® PP 0.45 µm filters.

Ion exchange chromatography

The ionic separations were carried out on Thermo Scientific™ Dionex™ ICS-2100 IC System* using Thermo Scientific™ Dionex™ IonPac™ AG11, AS11 (2 mm) column.

Eluent	KOH from 1 to 65 mM in 45 min with gradient
Eluent source	Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge, Thermo Scientific™ Dionex™ AERS™ 500 (2 mm) Suppressor[3]

Mass spectrometry

The MS analyses were carried out on Thermo Scientific™ Q Exactive™ Hybrid Quadrupole Orbitrap™ Mass Spectrometer using electrospray ionization in negative mode.

High resolution full-scan MS and top 3 data-dependent MS/MS data were collected at resolving power of 70,000 and 35,000 at FWHM m/z 200 respectively. Stepped HCD normalized collision energy (NCE): 30, 45, 60.

Results and discussion

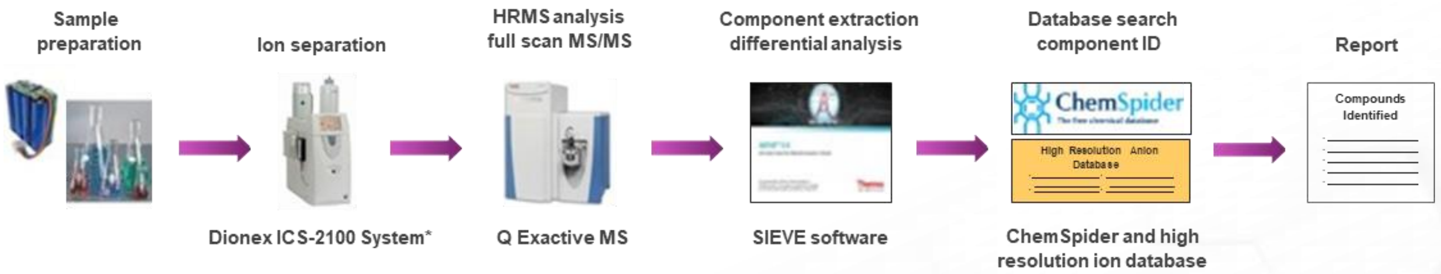
The anode samples were separated by the ICS-2100 system based on conductivity, and ions were eluted from the ion-exchange column based on their valences. The eluent was introduced to a

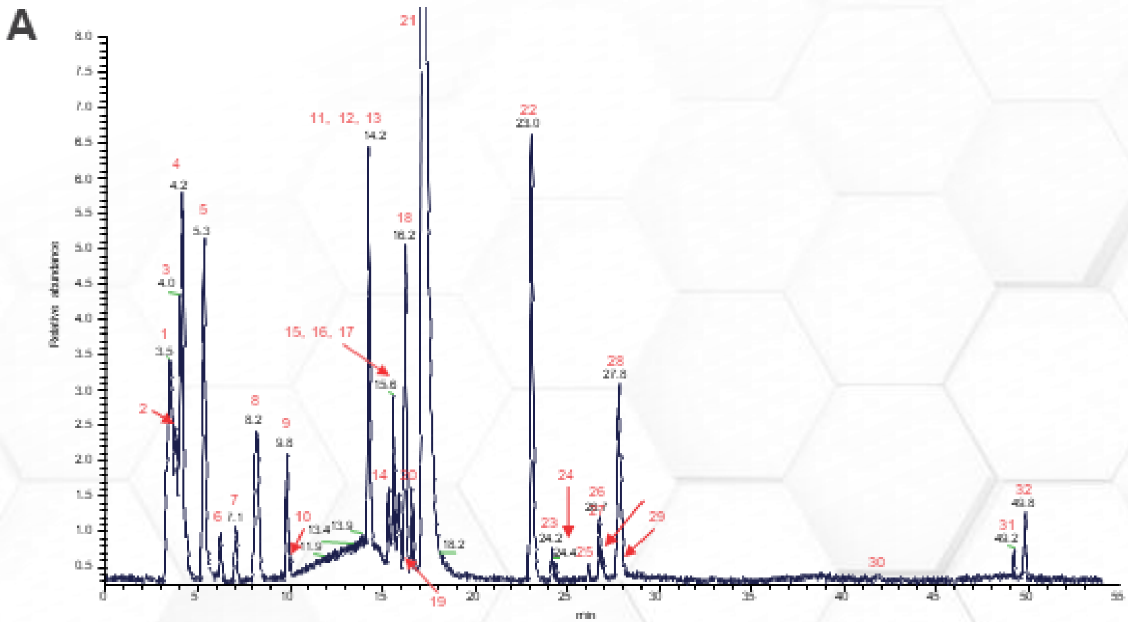
Sample preparation → Ion separation (Dionex ICS-2100 System*) → HRMS analysis full scan MS/MS (Q Exactive MS) → Component extraction differential analysis (SIEVE software) → Database search component ID (ChemSpider and high resolution ion database) → Report

Figure 1. Ion exchange chromatography and high resolution mass spectrometry workflow for lithium-ion battery anode impurity analysis

* or equivalent Thermo Scientific™ Dionex™ Integrion™ HPIC System

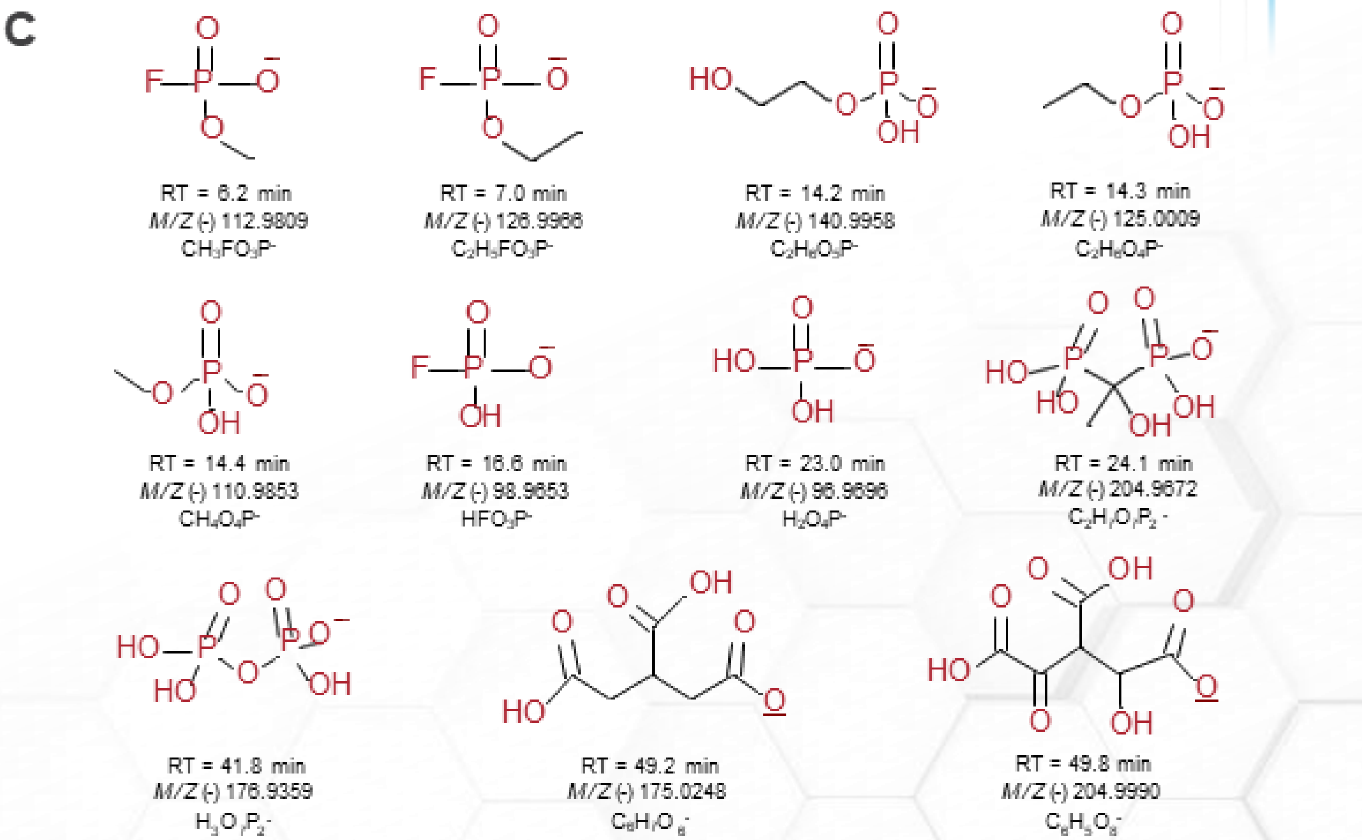
thermo scientific





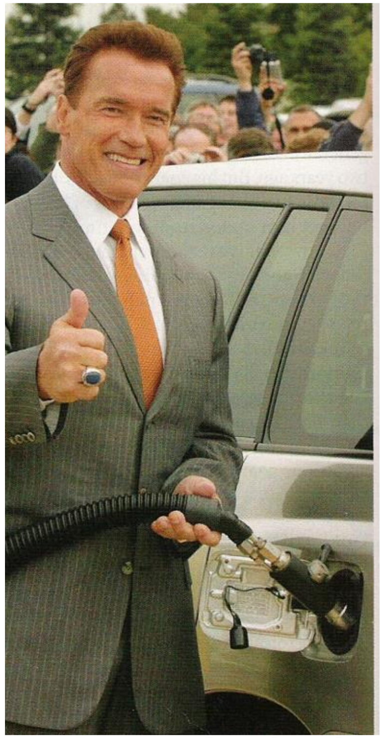
Li-Ion baterie – degradace elektrolytu – identifikace sloučenin

Components identified in cycle aged exhibited 20% loss in capacity—Sample 3					
Peak #	RT (min)	m/z	Formula (-)	Delta ppm	Name (based on MS results)*
1	3.2 - 3.6	125.0009 155.0116 169.0272 185.0222	$C_2H_6O_4P$ $C_3H_8O_5P$ $C_4H_{10}O_5P$ $C_4H_{10}O_6P$	0 0.6 0.6 0.6	Phosphate esters
2	3.8	139.0166	$C_3H_8O_4P$	0.4	Phosphoric acid
3	4.0	89.0244	$C_3H_5O_3$	0.1	
4	4.2	75.0088	$C_2H_3O_3$	- 0.2	Methyl carbonate
5	5.3	139.0071	$C_3H_7O_4S$	0.4	Propyl sulfate
6	6.2	112.9810	CH_3O_2FP	0.3	Methyl phosphorofluoridate
7	7.1	126.9966	$C_2H_5O_2FP$	0.1	Ethyl phosphorofluoridate
8	8.2	123.0122	$C_3H_7O_3S$	0.3	Propyl sulfonate
9	9.8	140.9864	$C_2H_5O_5S$	0.3	2- hydroxyethyl sulfate
10	10.0	155.0020	$C_3H_7O_5S$	-0.3	
11	14.2	140.9958	$C_2H_6O_5P$	0.1	2- hydroxyethyl hydrogen phosphate
12	14.3	125.0009	$C_2H_6O_4P$	-0.1	ethyl hydrogen phosphate
13	14.4	110.9853	CH_4O_4P	-0.2	methyl hydrogenphosphate
14	15.3	131.0350	$C_5H_7O_4$	0	3-carboxy-2-methylpropanoate
15	15.6	117.0193	$C_4H_5O_4$	0.2	methyl malonate
16	15.7	133.0143	$C_4H_5O_5$	0.2	3-carboxy-3-hydroxypropanoate
17	15.9	117.0194	$C_4H_5O_4$	0.2	Succinate
18	16.2	103.0037	$C_3H_3O_4$	0.3	2-carboxyacetate
19	16.6	98.9653	HO_2FP	0	hydrogen phosphorofluoridate
20	17.1	118.9986	$C_3H_3O_5$		
21	17.2	96.9601	HO_4S	- 0.2	hydrogen sulfate
22	23.0	96.9696	H_2O_4P	- 0.5	dihydrogen phosphate
23	24.2	204.9674	$C_2H_7O_7P_2$	0.7	hydrogen (1-hydroxy-1-phosphono-ethyl)-phosphonate
24	24.4	190.9517	$CH_5O_7P_2$	1.1	Methyl trihydrogen diphosphate
25	26.1	131.0349	$C_5H_7O_4$	-0.4	
26	26.7	175.0249	$C_6H_7O_6$	0.3	
27	26.9	147.0299	$C_5H_7O_5$	0.3	4-carboxy-3-hydroxybutanoate
28	27.8	161.0092	$C_5H_5O_6$	0.1	Ethanetricarboxylate
29	27.9	103. 0037	$C_3H_3O_4$	0	
30	41.7	176.9360	$H_3O_7P_2$	0.3	Trihydrogen diphosphate
31	49.2	175.0249	$C_6H_7O_6$	0.3	Tricarballylate
32	49.8	204.9312	$C_6H_5O_7$	0.1	



VODÍK

ZÁZRAK



NEBO

KATASTROFA

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Proč vodík?

- Přechod na bezemisní ekonomiku
- Nejrozšířenější prvek
- Dlouholeté využívání – vzducholodě, raketové palivo (Apollo), palivové články (ponorky, sondy), složka svítiplynu
- Palivo, ale také úložiště energie („přečerpávací elektrárna“) – vysoká hmotnostní energetická hustota

Kritické body

- Skladování
- Bezpečnost
- Čistota
- Cena palivového článku

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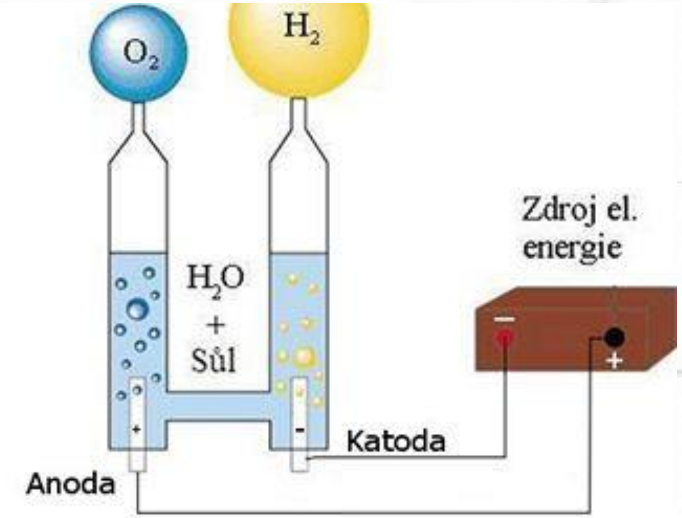
Výroba vodíku a jeho „barvy“

- 96% z fosilních paliv, zejména parní reforming zemního plynu
- 4% elektrolýzou

- Parní reforming – šedý vodík
- Parní reforming s CCS (Carbon Capture Storage) – **modrý vodík**
- Vedlejší produkt z výroby chloru – **bílý vodík**
- Elektrolýza elektřinou z obnovitelných zdrojů – **zelený vodík**



Vodík jako palivo a jeho analýza

- ČSN ISO **14687** - Kvalita vodíkového paliva
- ČSN ISO 21081 - Analýza vodíkových směsí
- ČSN 65 4435 - Technický stlačený plynný vodík

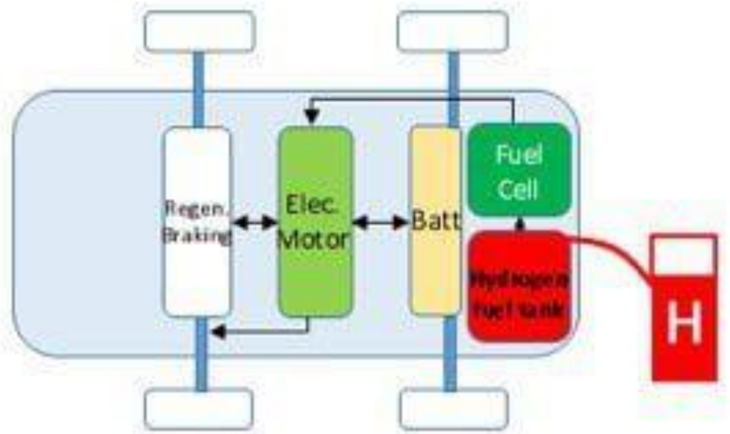
Constituent	Chemical Formula	Limits	Laboratory Test Methods to Consider and Under Development[e]	Minimum Analytical Detection Limit
Hydrogen fuel index	H_2	> 99.97%		
Total allowable non-hydrogen, non-helium, non-particulate constituents listed below		100		
Acceptable limit of each individual constituent				
Water[a]	H_20	5	**ASTM D7653-10, ASTM D7649-10**	0.12
Total hydrocarbons[b] (C_1 basis)		2	**ASTM D7675-11**	0.1
Oxygen	O_2	5	**ASTM D7649-10**	1
Helium		300	**ASTM D1945-03**	100
Nitrogen, Argon	N_2, Ar	100	**ASTM D7649-10**	5
Carbon dioxide	CO_2	2	**ASTM D7649-10, ASTM D7653-10**	0.1
Carbon monoxide	CO	0.2	**ASTM D7653-10**	0.01
Total sulfur[c]		0.004	**ASTM D7652-11**	0.00002
Formaldehyde	HCHO	0.01	**ASTM D7653-10**	0.01
Formic acid	HCOOH	0.2	**ASTM D7550-09 , ASTM D7653-10**	0.02
Ammonia	NH_3	0.1	**ASTM D7653-10**	0.02
Total halogenates[d]		0.05	(Work Item 23815)	0.01
Particulate Concentration		1 mg/kg	**ASTM D7650-10 , ASTM D7651-10**	0.005 mg/kg

Vodík jako palivo a jeho analýza

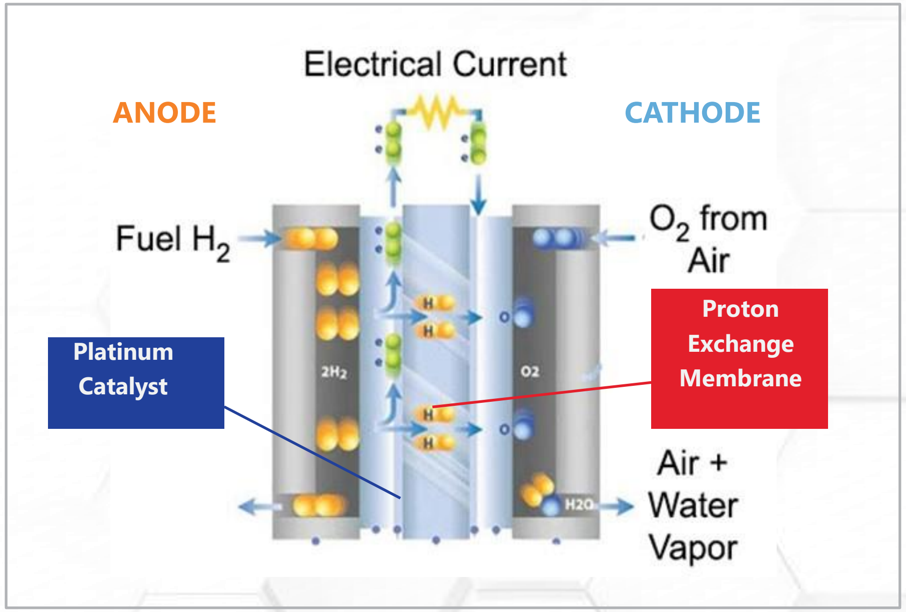
- „Auta na vodík“ - Fuel Cell Electric Vehicles (FCEVs)

Nádrž H2 - proton exchange membrane (PEM) – nabíjení

baterie - elektromotor



- **PEM velice citlivý na kvalitu vodíku**



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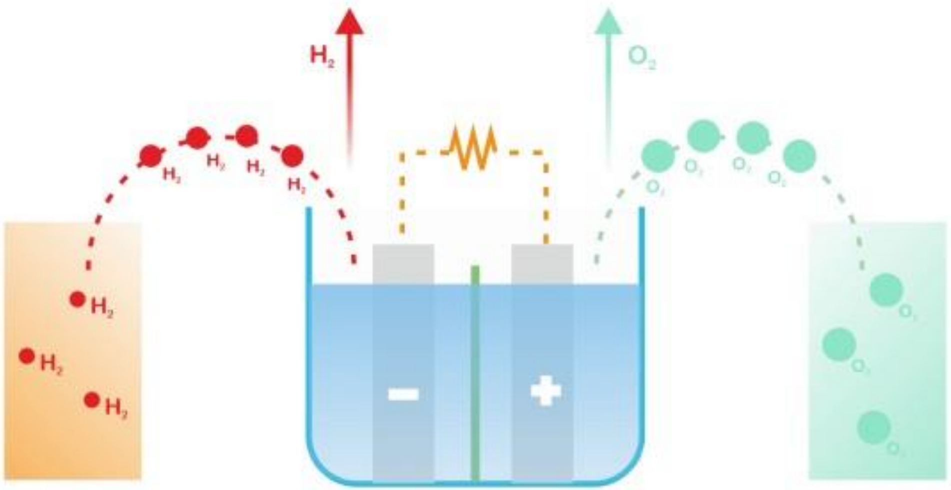
Vodík jako palivo a jeho analýza

- Parní reforming – **šedý vodík**
- Parní reforming s CCS (Carbon Capture Storage) – **modrý vodík**
- Vedlejší produkt z výroby chloru – **bílý vodík**

- **Elektrolýza** elektřinou z obnovitelných zdrojů – **zelený vodík** – **VELICE ČISTÝ PRODUKT – H_2**



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Vodík jako palivo a jeho analýza

Constituent	Chemical Formula	Limits	Laboratory Test Methods to Consider and Under Development[e]	Minimum Analytical Detection Limit
Hydrogen fuel index	H_2	> 99.97%		
Total allowable non-hydrogen, non-helium, non-particulate constituents listed below		100		
Acceptable limit of each individual constituent				
Water[a]	H_20	5	**ASTM D7653-10, ASTM D7649-10**	0.12
Total hydrocarbons[b] (C_1 basis)		2	**ASTM D7675-11**	0.1
Oxygen	O_2	5	**ASTM D7649-10**	1
Helium		300	**ASTM D1945-03**	100
Nitrogen, Argon	N_2, Ar	100	**ASTM D7649-10**	5
Carbon dioxide	CO_2	2	**ASTM D7649-10, ASTM D7653-10**	0.1
Carbon monoxide	CO	0.2	**ASTM D7653-10**	0.01
Total sulfur[c]		0.004	**ASTM D7652-11**	0.00002
Formaldehyde	HCHO	0.01	**ASTM D7653-10**	0.01
Formic acid	HCOOH	0.2	**ASTM D7550-09 , ASTM D7653-10**	0.02
Ammonia	NH_3	0.1	**ASTM D7653-10**	0.02
Total halogenates[d]		0.05	(Work Item 23815)	0.01
Particulate Concentration		1 mg/kg	**ASTM D7650-10 , ASTM D7651-10**	0.005 mg/kg

Vodík jako palivo a jeho analýza

Water - chilled mirror hygrometer (dew point meter); quartz crystal microbalance; CRDS; Capacitance, Continuous wave CRDS; **GC**-MS; GC-MS with jet pulse injection; FTIR

THC – **GC**-FID; Methanizer GC-FID; GC-MS with pre-concentrator; FTIR

Oxygen – Electrochemical sensor; **GC**-MS with jet pulse injection; GC-TDC; GC-PDHID; Continuous wave CRDS

Helium – **GC**-TCD

Nitrogen – **GC**-TCD; GC-PDHID; GC-MS with jet pulse injection

Argon - **GC**-TCD; GC-PDHID; GC-MS with jet pulse injection

Carbon dioxide - Methanizer **GC**-FID; GC-PDHID; GC-MS with jet pulse injection; FTIR; Continuous wave CRDS

Carbon monooxide - **GC**-PDHID; Methanizer GC-FID; FTIR; Continuous wave CRDS

Total sulphur – **GC**-SCD with pre-concentrator; GC-FPD with pre-concentrator, GC-SCD without pre-concentrator

Formaldehyde - **GC**-MS with pre-concentrator; GC-MS without pre-concentrator; Continuous wave CRDS

Formic acid – FTIR; IC with impinger sampling device; **GC**-MS

Ammonia – **GC**-MS; FTIR; IC; IC with impinger sampling device; Continuous wave CRDS

Total halogenates - IC with impinger sampling device; **GC**-MS with pre-concentrator

Vodík jako palivo a jeho analýza

Celková – ***různými metodami, popř. ve více různých laboratořích - analýza všech kontaminantů s dostatečnou citlivostí***

Částečná – ***analýza části kontaminantů, mnohdy s nižší citlivostí***

CDRS – H_2O, CO_2, CO, CH_4, NH_3, CH_2O, O_2 - používá se v J. Koreji u vodíkových stanic

GC-FID+TCD+methanizer – THC, O_2, He, N_2, Ar, CO_2, CO

GC-TCD + FTIR - O_2, He, N_2, Ar, H_2O, THC, CO, CO_2, CH_2O, HCOOH, NH_3

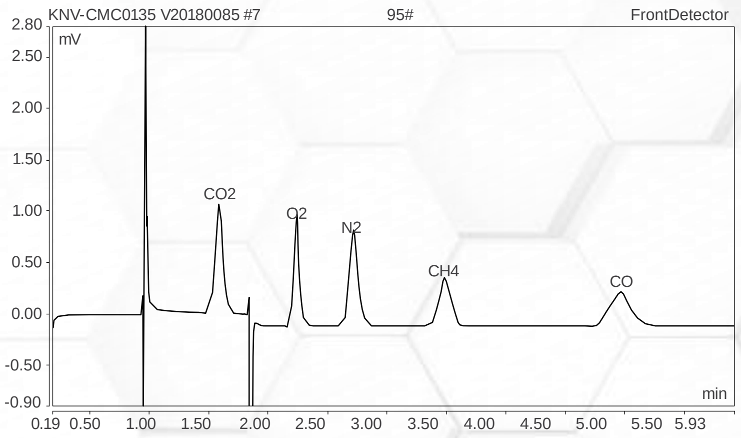

Figure 1. Representative chromatogram of a Permanent Gas Standard at 500 ppm using TCD channel with Helium carrier gas

CITLIVOST A DETEKČNÍ LIMITY!!!

Anebo…

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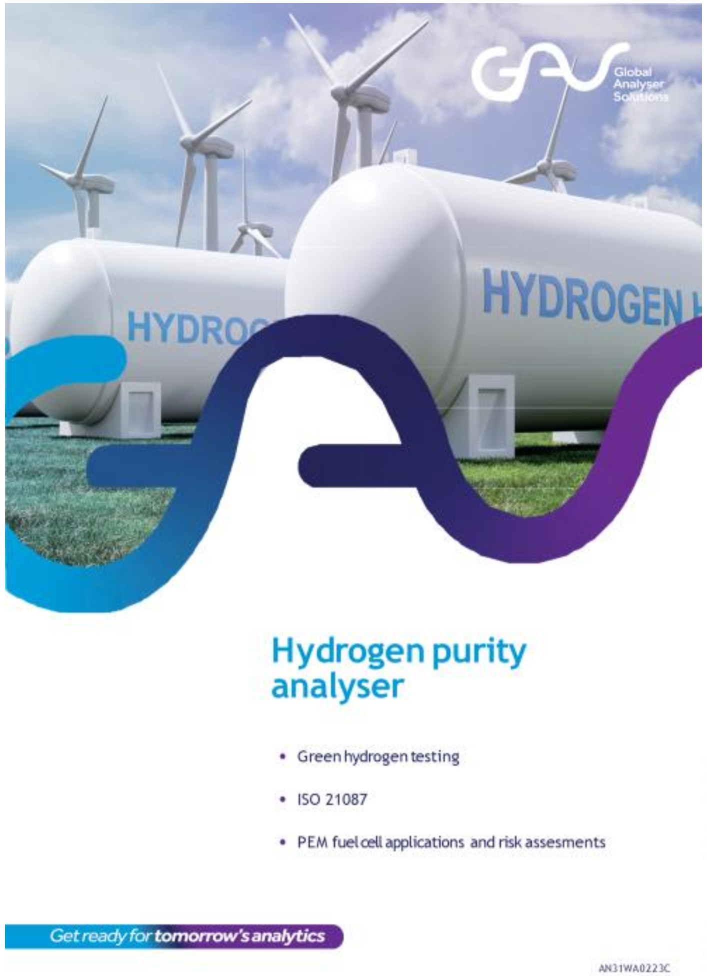
KOMPLEXNÍ ŘEŠENÍ SPOLEČNOSTI G.A.S.

Jeden přístroj s mnoha moduly, instalace, spuštění, měření, podpora, jednotlivé moduly od výrobceTHERMO SCIENTIFIC

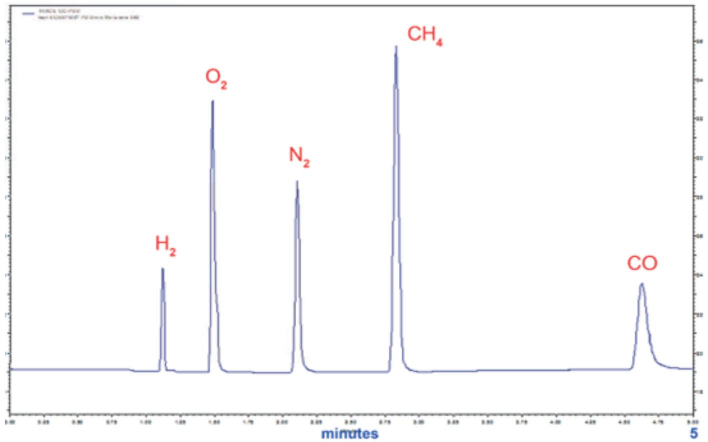


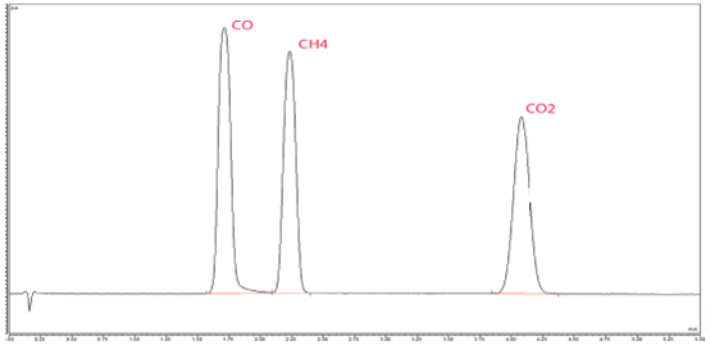
Impurity	Limit 21087 (umol/mol)	GAS GC method	Detection range
Total hydrocarbons	2	MS-AEI	0.1-1000
Oxygen	5	PDD	0.02-1000
Helium	300	TCD	50-10000
Nitrogen	100	PDD	0.02-1000
Argon	100	PDD	0.02-1000
Carbon dioxide	2	Methaniser-FID	0.05-1000
Carbon monoxide	0.2	Methaniser-FID	0.05-1000
Total sulphur components	0.004	MS-AEI	0.0001-100 (per comp.)
Formaldehyde	0.01	MS-AEI	0.005-100
Ammonia	0.1	MS-AEI	0.1-100
Halogenated components	0.05	MS-AEI	0.001-100

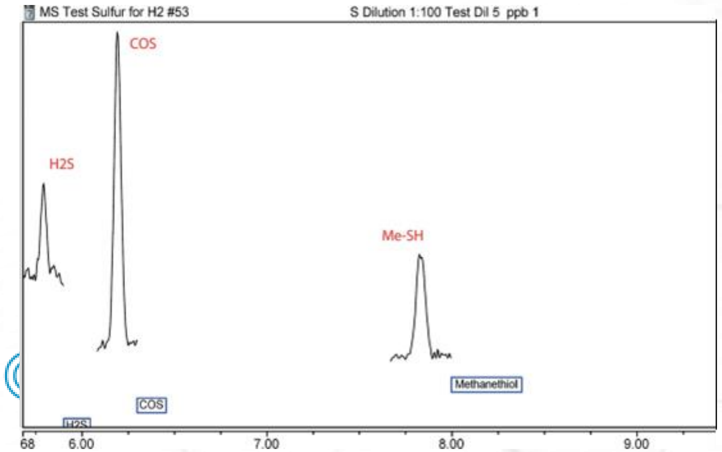
KOMPLEXNÍ ŘEŠENÍ SPOLEČNOSTI G.A.S.

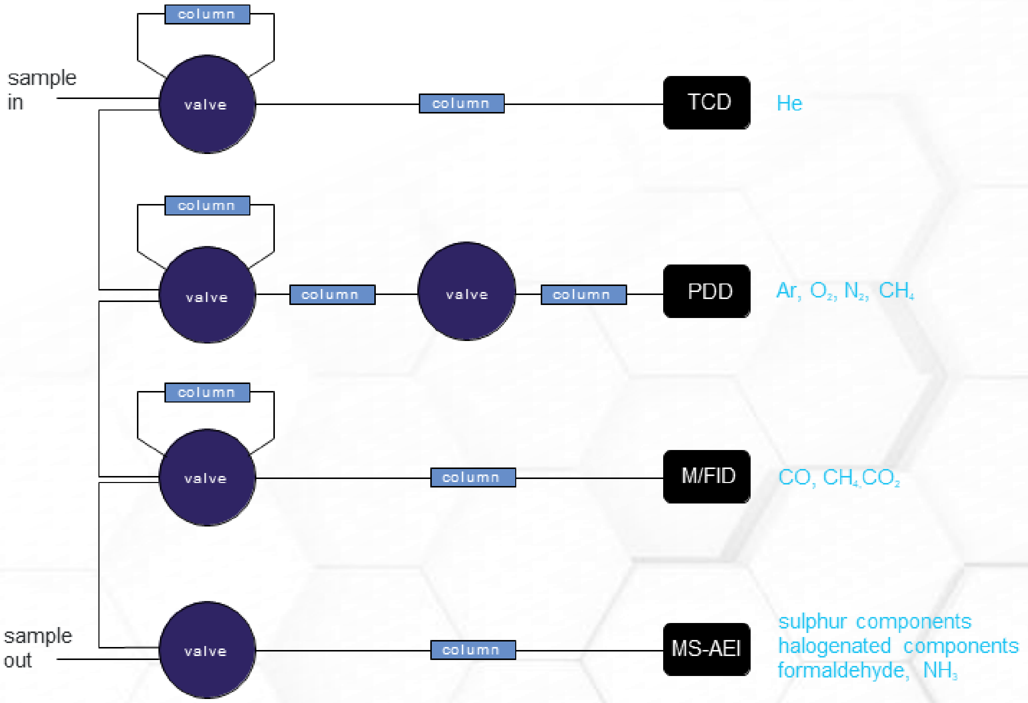
Jeden přístroj, tři moduly. Instalace, spuštění, měření, podpora.

Analýza téměř všech analytů a s dostatečnou citlivostí.









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SHRNUTÍ

Analýza alternativních zdrojů energie je možná i ve Vaší laboratoři!!!

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