Workshop -Flow batteries, bringing the technology to the market

Vitoria-Gasteiz

Jan Svoboda, Petr Mazúr, Václav Čmolík, Jiří Charvát,

UWB Pilsen, UCT Prague

Characterization of AORFB

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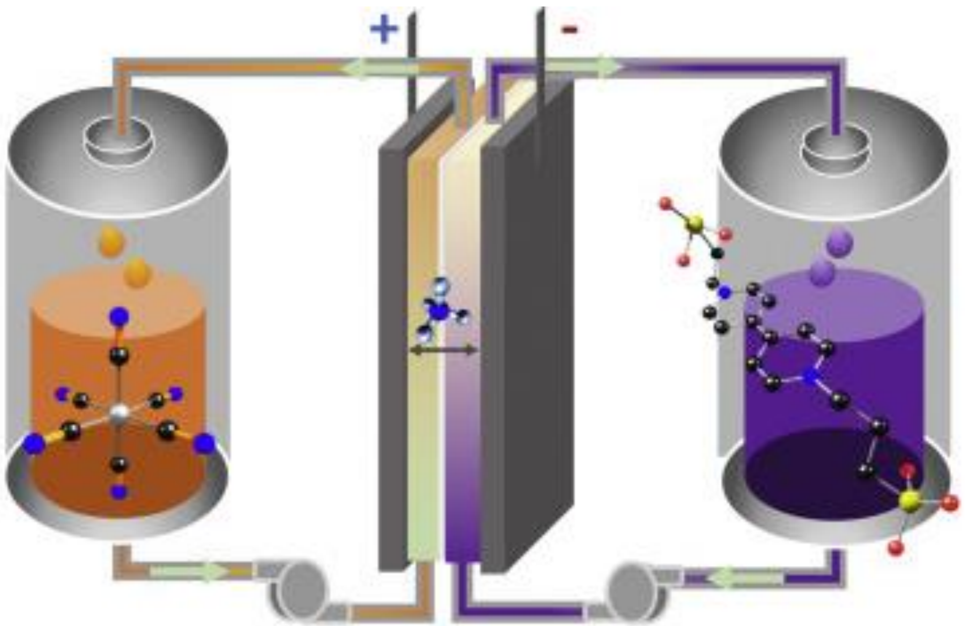
Introduction

- Optimisation of electrolyte composition
  - Comparision of mixed and non-mixed electrolyte
- Oxygen permeation
- Effect of flow rate
- Effect of SOC



$K_4Fe(CN)_6$ posilyte

SPr_2V anolyte

J. Luo et al., Joule (3), Issue 1, 2019, 149-163

RFB tests: Experimental

Experimental conditions:	
Electrodes	GFD4.6 EA (4,6 um thick, 4 cm2 active area)
Membrane	FSXX0 (Fumatech, dry)
Anolyte	XM V(SPr)2 in XM XCl 15 ml (0% SOC)
Catholyte	XM X4Fe(CN)6 in H2O 20 ml (0% SOC)*
Atmosphere	Under 5.0 nitrogen

NOTE: Catholyte was always of same concentration of active species as anolyte and without supporting salts.

Procedure:	
Characterization	EIS + load curves (50% SOC), various flow rates (40 ml min-1)
Capacity evaluation	CC-CV cycling (100 mA cm-2, 0.3-1.0 V cut-offs, 2c)
Current density	CC cycling (125, 100, 75 and 50 mA cm-2, 0.3-1.1 V cut-offs)
Characterization	EIS + load curves (50% SOC), various flow rates
Stability test	CC cycling (100 mA cm-2, 0.3-1.1. V, 50c)
Capacity evaluation	CC-CV cycling (100 mA cm-2, 2c)
Characterization	EIS + load curves (50% SOC), various flow rates (40 ml min-1)

NOTE: Sometime, final testing was performed after catholyte exchange for fresch one to see the anolyte capacity decay.

Slide 3

RFB TESTS: CELL POLARIZATION

Negolyte composition	Membrane	Rohm (Ω cm^2)	Rohm (%)	Rchar (Ω cm^2)	Rdis (Ω cm^2)
0.9M SPr2V in 3M NH4Cl	FS-950	1.16	85%	1.32	1.37
0.75M SPr2V in 2M NH4Cl	FS-950	1.84	92%	2.10	1.99
0.75M SPr2V in 2M KCl	FS-950	2.64	86%	2.68	3.08
0.9M SPr2V in 2M NaCl/KCl	FS-950	2.04	87%	2.16	2.34
1.1M SPr2V in 2M NaCl/KCl	FS-950	1.16	86%	1.48	1.35
1.1M SPr2V in 2M NH4Cl	FS-950	0.86	81%	1.06	1.06

LC in +50% SOC, SGL 46EA, 4 cm2, 40 ml/min, RT
GB... nitrogen-filled glove-box
act... membrane activated (1h in H_2O 60°C, 1h in H_2O 80°C)

RFB TESTS: CELL CYCLING

Negolyte composition	Membrane	CE (%)	VE (%)	EE (%)	CU (%)	CD (%Qteo)
0.9M SPr2V in 3M NH4Cl	FS-950	99.2	68.8	68.3	91	-12.6
0.75M SPr2V in 2M NH4Cl	FS-950	99.1	55.1	54.6	86	-20.4
0.75M SPr2V in 2M KCl	FS-950	99.3	42.4	42.1	76	Cathode failure
0.9M SPr2V in 2M NaCl/KCl	FS-950	99.4	50.7	50.4	75	-10.3
1.1M SPr2V in 2M NaCl/KCl	FS-950	99.5	57.3	57.0	84	-17.8
1.1M SPr2V in 2M NH4Cl	FS-950	99.2	72.5	71.9	87	-17.1*

LC in +50% SOC, SGL 46EA, 4 cm2, 40 ml/min, RT
GB... nitrogen-filled glove-box
act... membrane activated (1h in H_2O 60°C, 1h in H_2O 80°C)

* Partially due to posilyte leak, only 3% decay after posilyte exchange.

RFB TESTS: CELL POLARIZATION

Negolyte composition	Membrane	Rohm (Ω cm^2)	Rohm (%)	Rchar (Ω cm^2)	Rdis (Ω cm^2)
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	**FS-950**	3.00	95%	3.12	3.17
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	**FS-830**	1.80	87%	2.11	2.08
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	**FS-730**	1.44	84%	1.73	1.72
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl (GB)	**FS-730**	0.80	76%	1.03	1.05
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	**FS-730 (act)**	0.56	67%	0.83	0.83
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	**FS-720**	0.60	68%	0.88	0.88

LC in +50% SOC, SGL 46EA, 4 cm2, 40 ml/min, RT
GB... nitrogen-filled glove-box
act... membrane activated (1h in H_2O 60°C, 1h in H_2O 80°C)

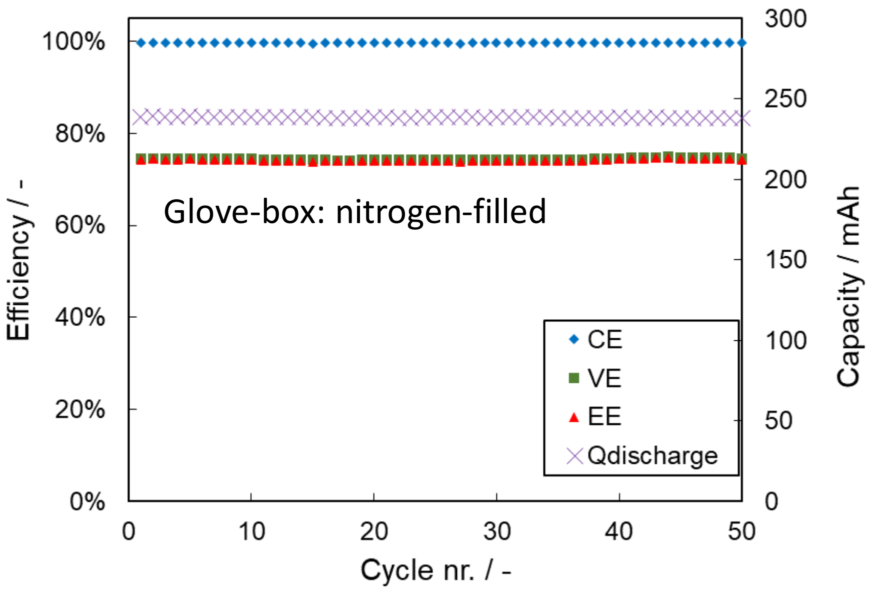
RFB TESTS: CELL CYCLING

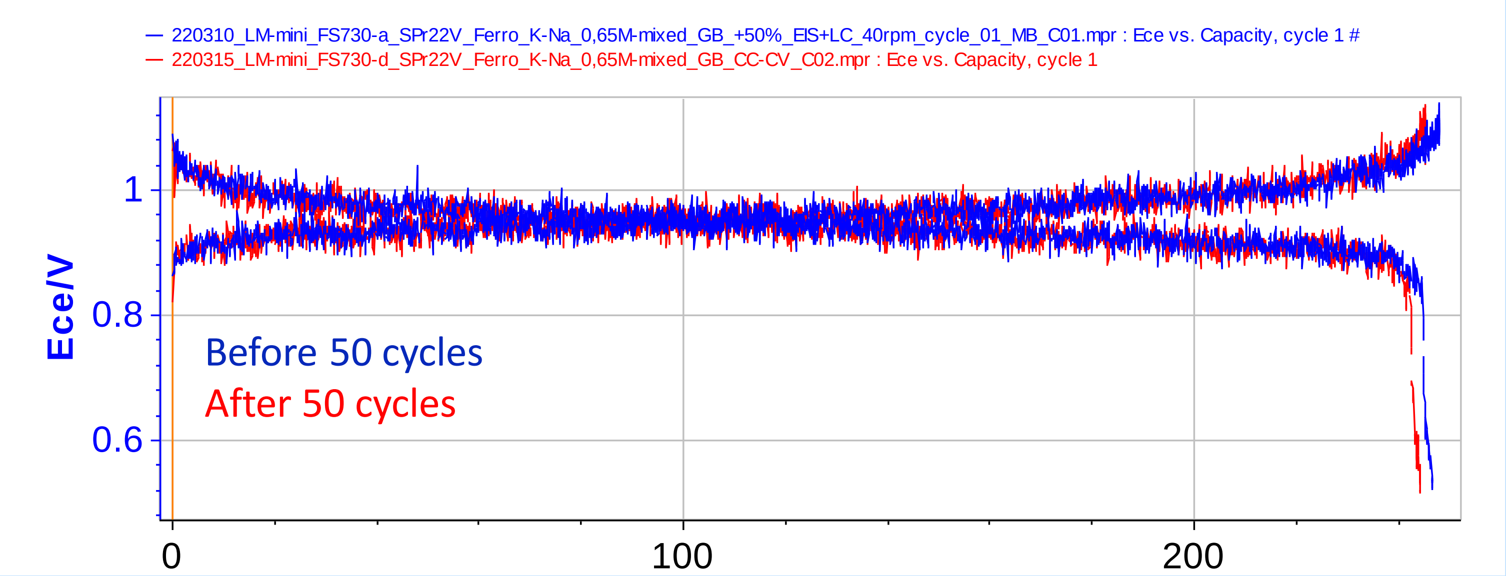
Negolyte composition	Membrane	CE (%)	VE (%)	EE (%)	CU (%)	CD (%Qteo)
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	FS-950	99.4	46.8	46.5	88	-5.0
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	FS-830	99.1	58.3	57.7	86	-22.6
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	FS-730	99.4	62.2	61.8	89	-5.0
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl (GB)	FS-730	99.7	74.4	74.2	92	-0.2
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	FS-730 (act)	99.0	79.1	78.3	95	-2.5
0.65M K-Na-FeCN + 0.65M SPr2V + 0.5M NH4Cl	FS-720	98.5	76.3	75.1	92	-13.3

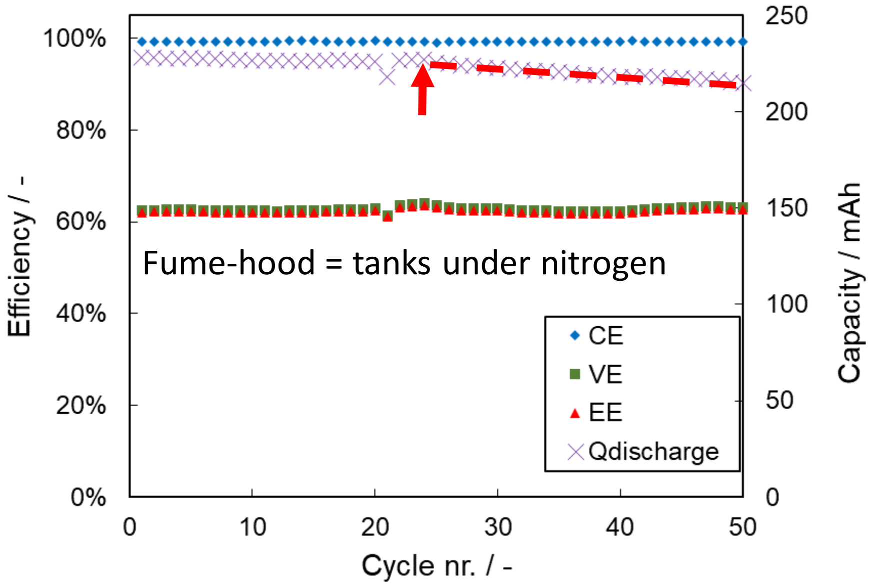
LC in +50% SOC, SGL 46EA, 4 cm2, 40 ml/min, RT
GB... nitrogen-filled glove-box
act... membrane activated (1h in H_2O 60°C, 1h in H_2O 80°C)

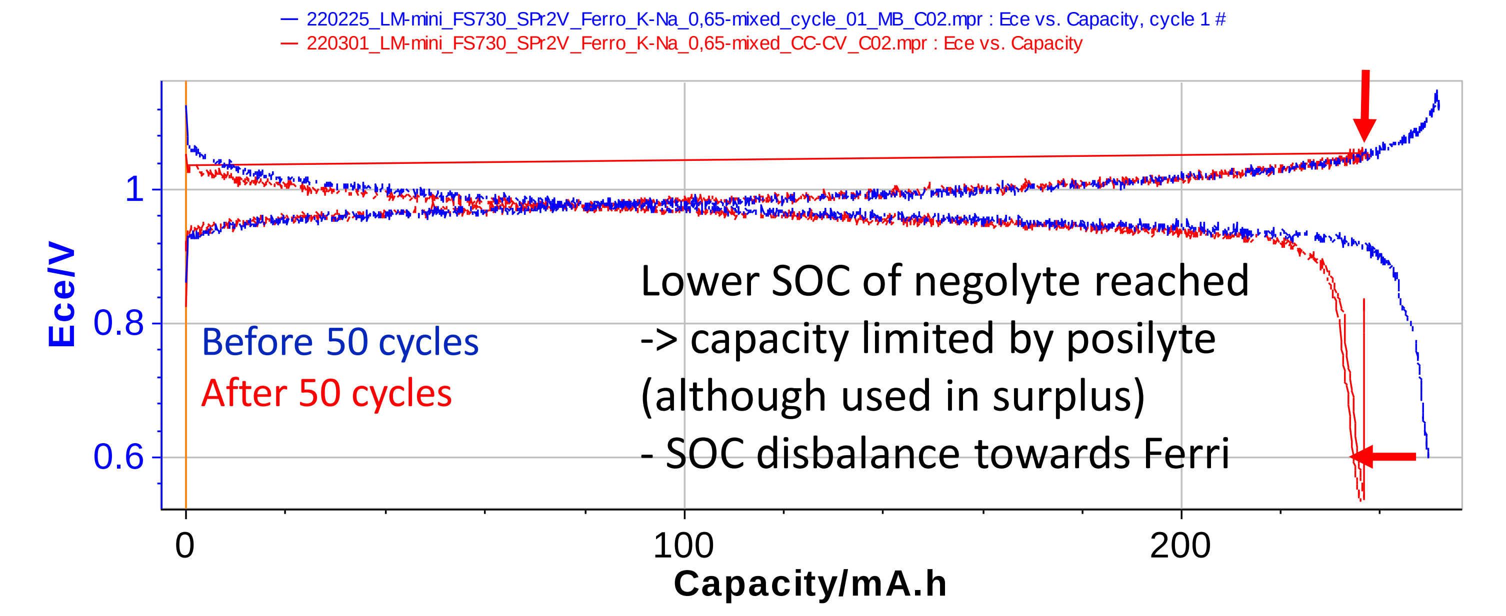
RFB TESTS: CELL CYCLING

Negative electrode potential during CC-CV



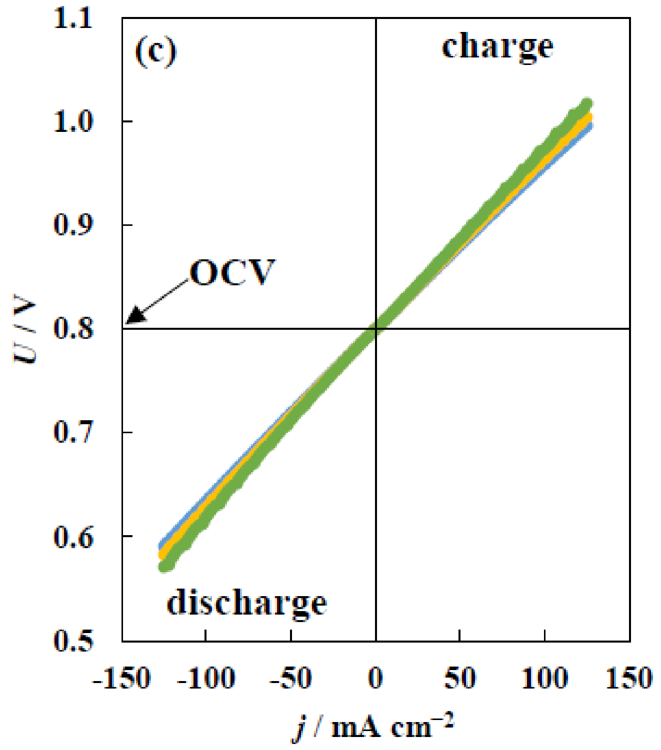




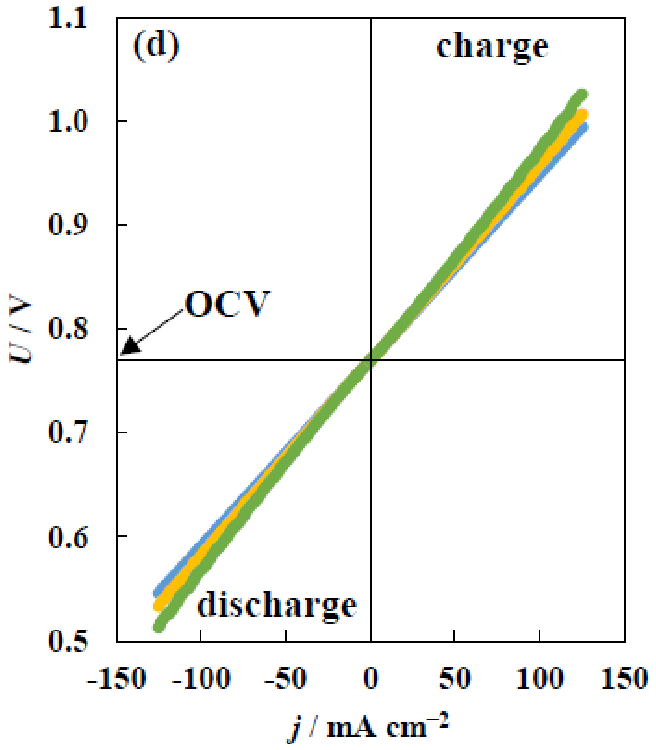


Battery testing – EIS + load cruves

Non – mixed electrolyte



Mixed electrolyte

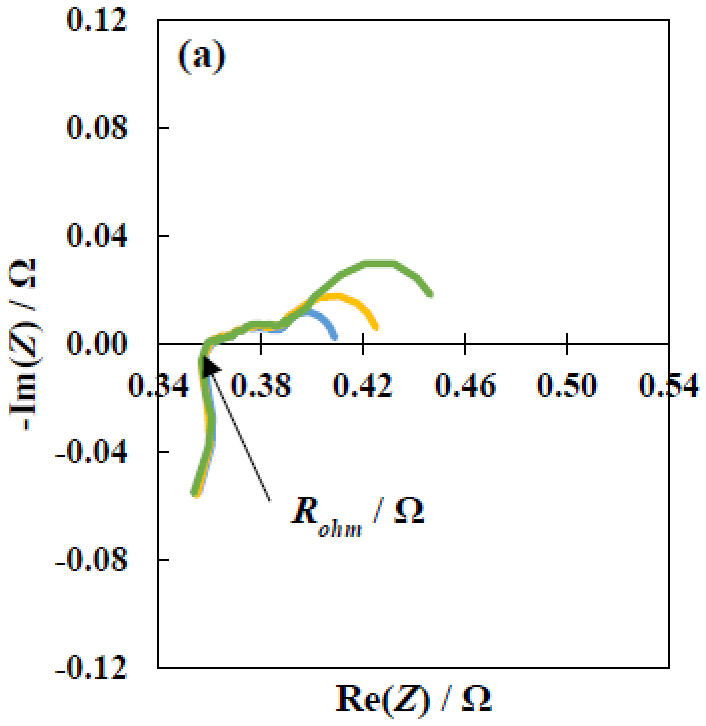


Electrolyte		non-mixed	
Flowrate / $cm^3\ min^{-1}$	40	20	10
ASR_{ohm} / $\Omega\ cm^2$	1.44	1.44	1.44
ASR_{char} / $\Omega\ cm^2$	1.58	1.65	1.75
ASR_{dis} / $\Omega\ cm^2$	1.67	1.74	1.85
ASR_{ohm}/ASR_{dis}	86%	83%	78%

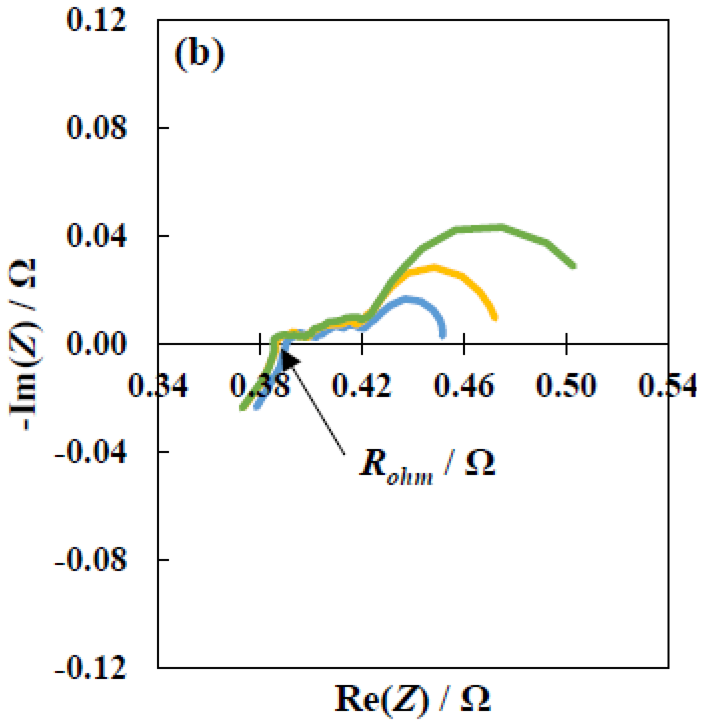
Electrolyte		mixed	
Flowrate / $cm^3\ min^{-1}$	40	20	10
ASR_{ohm} / $\Omega\ cm^2$	1.56	1.55	1.54
ASR_{char} / $\Omega\ cm^2$	1.80	1.90	2.07
ASR_{dis} / $\Omega\ cm^2$	1.79	1.90	2.06
ASR_{ohm}/ASR_{dis}	87%	82%	75%

Battery testing – EIS + load cruves

Non – mixed electrolyte



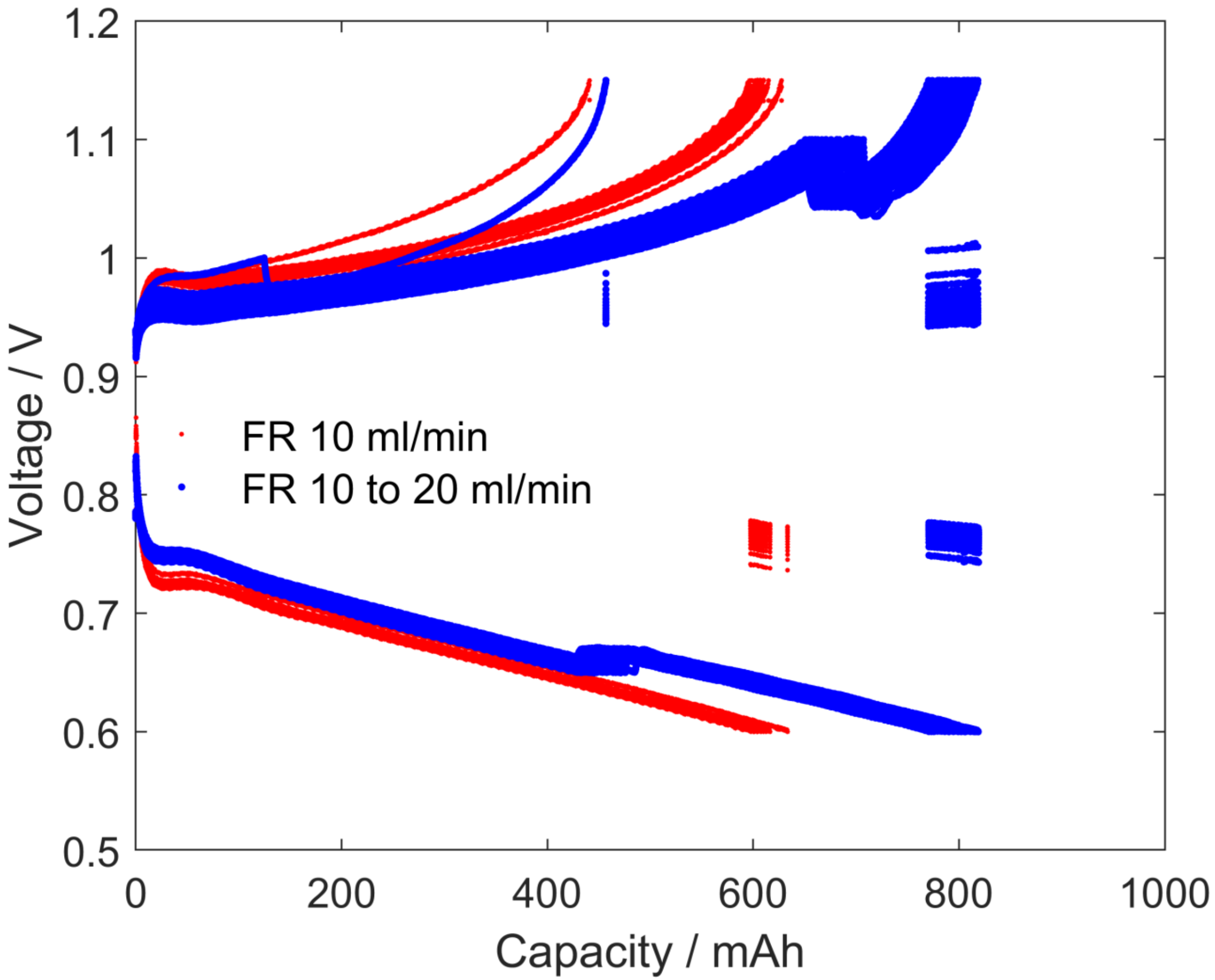
Mixed electrolyte



Electrolyte	non-mixed		
Flowrate / $cm^3\ min^{-1}$	40	20	10
ASR_{ohm} / $\Omega\ cm^2$	1.44	1.44	1.44
ASR_{char} / $\Omega\ cm^2$	1.58	1.65	1.75
ASR_{dis} / $\Omega\ cm^2$	1.67	1.74	1.85
ASR_{ohm}/ASR_{dis}	86%	83%	78%

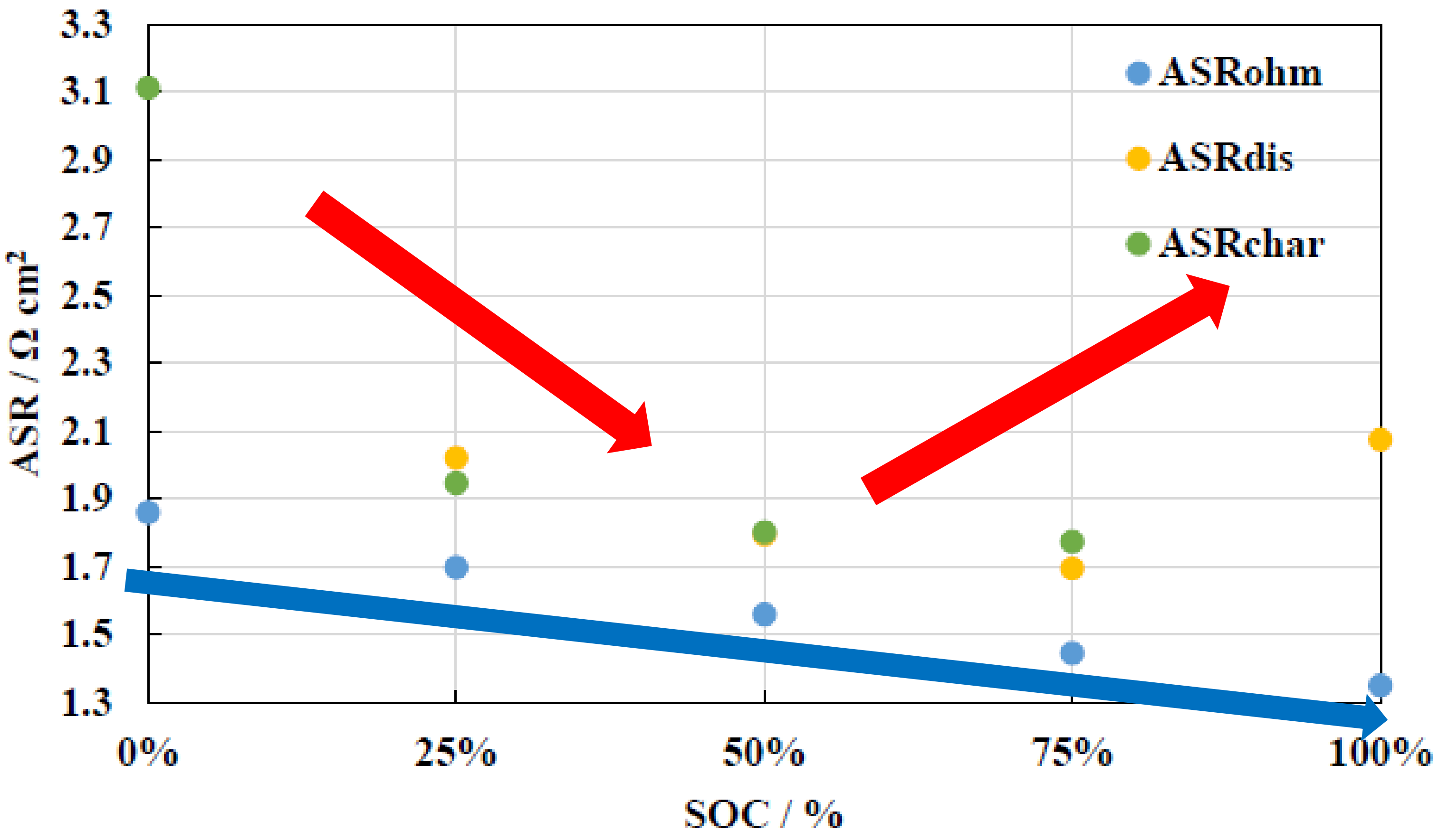
Electrolyte	mixed		
Flowrate / $cm^3\ min^{-1}$	40	20	10
ASR_{ohm} / $\Omega\ cm^2$	1.56	1.55	1.54
ASR_{char} / $\Omega\ cm^2$	1.80	1.90	2.07
ASR_{dis} / $\Omega\ cm^2$	1.79	1.90	2.06
ASR_{ohm}/ASR_{dis}	87%	82%	75%

Effect of flow rate



- Increase of capacity utilization by 25 % when flow rate is doubled for last 50 mV

Effect of SoC - mixed

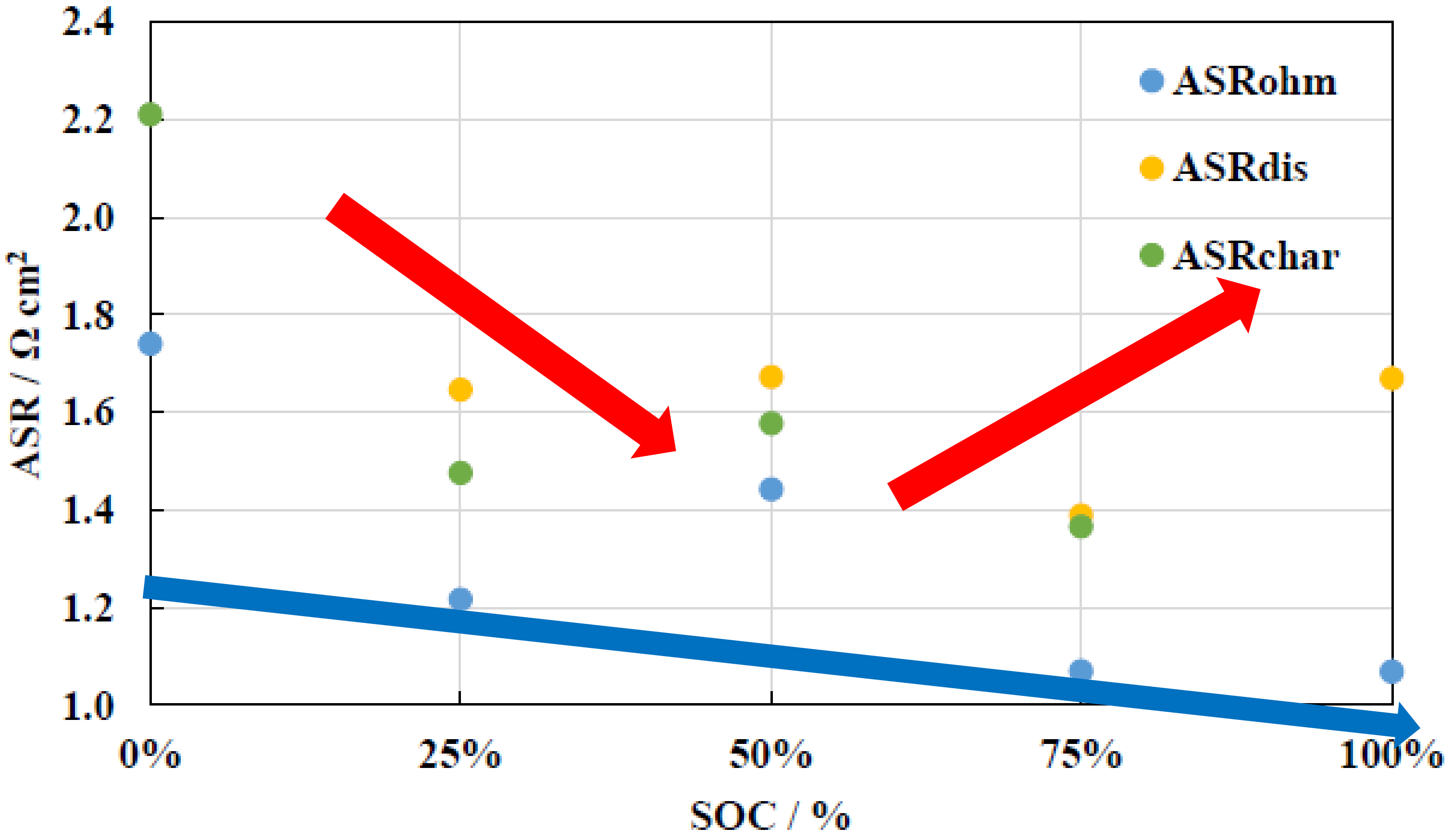


Increasing SoC

- Ohmic resistance is decreasing - conductivity
- Charge transfer resistence is increasing- conductivity

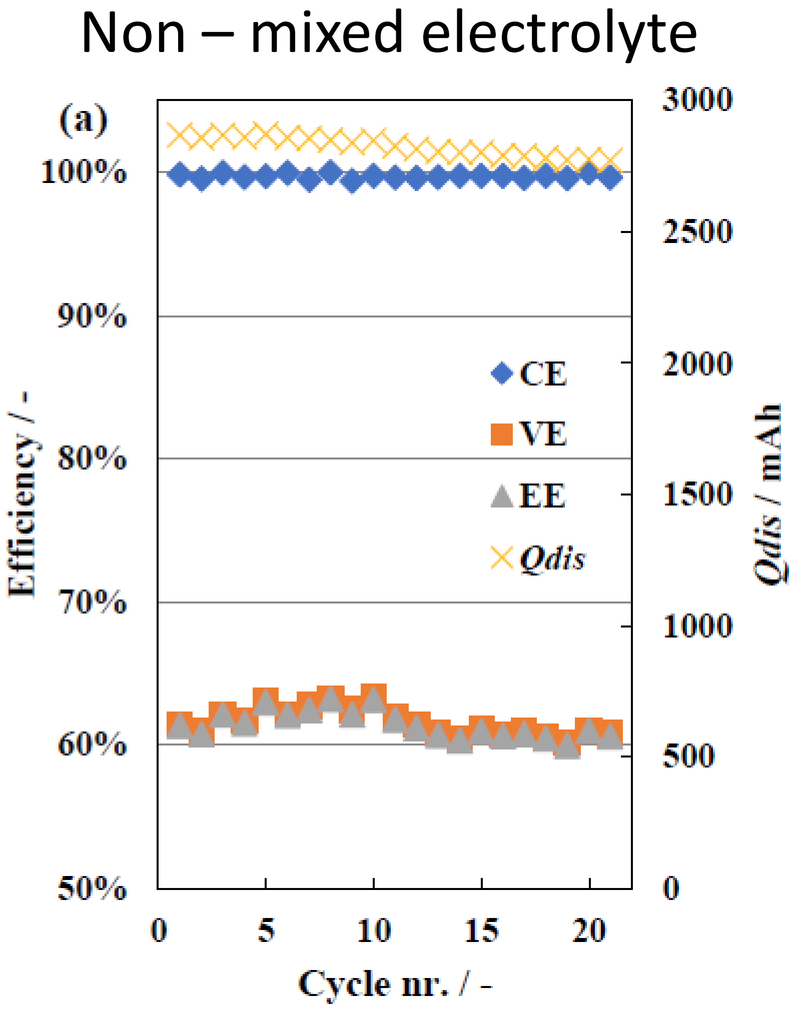
$$j_0 = nFk_0 c_{ox}{}^{\alpha} c_{red}{}^{1-\alpha}$$

Effect of SoC – non-mixed

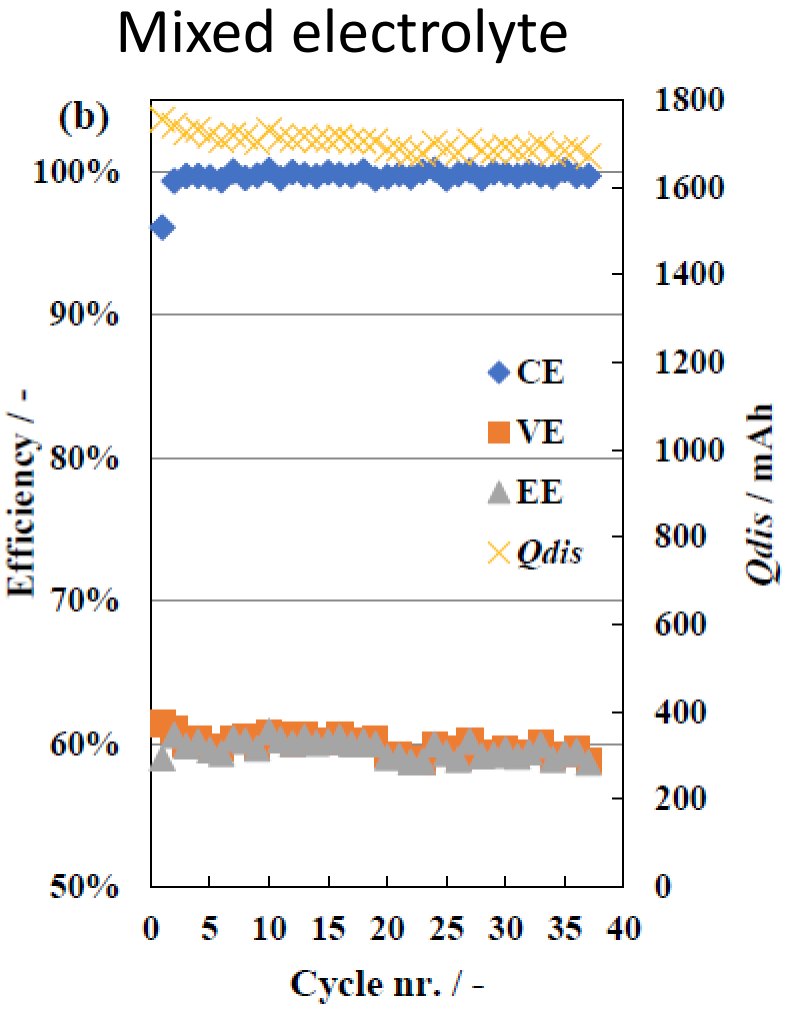


Probably temperature effect for 50 %SoC

Cycles



Non – mixed electrolyte
(a)
100%
90%
80%
70%
60%
50%
3000
2500
2000
1500
1000
500
0
CE
VE
EE
Qdis
Efficiency / -
Qdis / mAh
0
5
10
15
20
Cycle nr. / -



Mixed electrolyte
(b)
100%
90%
80%
70%
60%
50%
1800
1600
1400
1200
1000
800
600
400
200
0
CE
VE
EE
Qdis
Efficiency / -
Qdis / mAh
0
5
10
15
20
25
30
35
40
Cycle nr. / -

Cycles

Electrolyte	Cycle	CE	VE	EE	Q_{dis}	Q_{theo}	CU
		%	%	%	mAh	mAh	%
non-mixed	the first	98.4	63.8	62.8	3221	3602	89.4
non-mixed	the last	100.2	60.0	60.1	2907	3602	80.7
mixed	the first	98.8	63.0	62.2	1966	2091	94.0
mixed	the last	99.6	59.1	58.9	1906	2091	91.2

Electrolyte	Cycles	CE	VE	EE	Q_{dis}	Q_{theo}	CU	dQ/dc	dQ/day
		%	%	%	mAh	mAh	%	%Q_{theo}	%Q_{theo}
non-mixed	21	99.7	61.6	61.4	2872	3602	79.7	-0.13	-0.010
mixed	37	99.7	59.9	59.7	1755	2091	84.0	-0.11	-0.009

Conclusions

- Analytical model of shunt current losses and pressure losses and CFD model were developed
- Effect of flow rate is significant mainly significant
- Increase of flow rate at the end of cycle might significatnly increase capacity utilization
- Effect of electrolyte SoC on the resistence of the cell was examined

Thank you!

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