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Major Goals: Much of the interest for ionic liquids has been centered on their possible use as alternatives to volatile organic solvents, because they are considered as non-volatile and consequently non- flammable at ambient and higher temperatures. Ionic liquids can play the role of both solvents and electrolytes in electrochemical reactions. As ionic liquid components can be used as electrochemically active couples, we can take advantage of a maximum concentration of active species for high energy density. Ionic liquid flow battery based on the AlCl3: 1-ethyl-3-methyl imidazolium chloride (EMI-AlCl4) has already been described in the literature. During charging acidic chloroaluminate melt is fed into the battery. The acidic chloroaluminate in 1.5:1 molar ratio contains AlCl4- and Al2Cl7- species, Cl2 is produced at the positive electrode, while Al is plated on the negative electrode during charging reactions:
4AlCl4- ? Cl2 + 2Al2Cl7- + 2e-
4Al2Cl7-+ 3e- ? Al + 7AlCl4-
This work focused on enabling the use of halogenoaluminate for redox flow batteries by carrying out fundamental research on positive electrode couple. Since the acidic halogenoaluminate melt is highly corrosive, it is necessary to find a highly durable, competitive electrode material for electrochemical applications. Beside the durability, we need to find also an electrode and/or an appropriate electrocatalyst which ensures less overpotential and results higher current density for halide reduction/oxidation.

Accomplishments: Most of the electrode materials, carbon supports studied resist to the corrosion in bromoaluminate, no visible disintegration was observed.
- Graphite based supports were found to be the electrodes with the best performance from the electrochemistry of 2Br -/Br2 point of view:
• graphite sponge
• pyrolytic graphite sheet
• graphitized carbonpaper (Spectracarb)
- Substrates with high surface area, porous supports are favorable
- Performance can be enhanced significantly by Ru electrocatalyst deposition on the substrates
- Surface modification by pyrolytic graphite powder and KetjenBlack blend can improve the performance
Still needs to be working on:
- Long-term maintainable performance and stability because of either
• Electrode passivation/degradation/dissolution or

- No reversibility observed under cyclic voltammetric conditions or
- Slow aluminate solidification. One of the reasons for this can be the

hygroscopic behavior of the aluminate. Halogenation of the imidazolium ring can't be excluded leading to products with higher molecular weight and lower melting point.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

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Technology Transfer: Nothing to Report

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Final Report for Army Research Office

Agreement Number W911NF-16-1-0451

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Enabling Science for Redox Flow Batteries based on Room Temperature Ionic Liquids

Research Opportunity Number: W911NF-12-R-0012-02

(Paragraph 7 .2, Electrochemistry)

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For work completed September 30, 2017

Much of the interest for ionic liquids has been centered on their possible use as alternatives to volatile organic solvents, because they are considered as non-volatile and consequently non-flammable at ambient and higher temperatures. Ionic liquids can play the role of both solvents and electrolytes in electrochemical reactions. As ionic liquid components can be used as electrochemically active couples, we can take advantage of a maximum concentration of active species for high energy density. Ionic liquid flow battery based on the $AlCl_3$: 1-ethyl-3-methyl imidazolium chloride (EMI-$AlCl_4$) has already been described in the literature. During charging acidic chloroaluminate melt is fed into the battery. The acidic chloroaluminate in 1.5:1 molar ratio contains $AlCl_4^-$ and $Al_2Cl_7^-$ species, Cl_2 is produced at the positive electrode, while Al is plated on the negative electrode during charging reactions:

$$4AlCl_4^- \leftrightarrow Cl_2 + 2Al_2Cl_7^- + 2e^-$$

$$4Al_2Cl_7^- + 3e^- \leftrightarrow Al + 7AlCl_4^-$$

This work focused on enabling the use of halogenoaluminate for redox flow batteries by carrying out fundamental research <u>on positive electrode couple</u>. Since the acidic halogenoaluminate melt is highly corrosive, it is necessary to find a highly durable, competitive electrode material for electrochemical applications. Beside the durability, we need to find also an electrode and/or an appropriate electrocatalyst which ensures less overpotential and results higher current density for halide reduction/oxidation.

Basic cyclic voltammetric study of acidic chloro/bromoaluminate melts

During present project the first part of the experimental work was intended to the basic cyclic voltammetric study of the $AlCl_3$:EMICl in 1:1.5 molar ratio on platinum (Pt) and glassy carbon (GC) electrodes. The electrochemical potential window has been determined: as aluminum plating/stripping took place in the range of -0.2 – +0.2 V at Pt electrode (not shown in Fig. 1), chlorine evolution took place at potential higher than +2.2 V, however, this process seemed to be irreversible on both electrodes. A reduction peak observed at +1.1 V only on Pt electrode was assigned to the proton reduction. The organic cation was electrochemically inert in the potential range studied in the range of -0.5V - +3.0 V. On glassy carbon electrode irreversible chlorine evolution took place at higher anodic potential (more than +2.5 V) and no proton reduction was observed at all because of the higher overpotential.

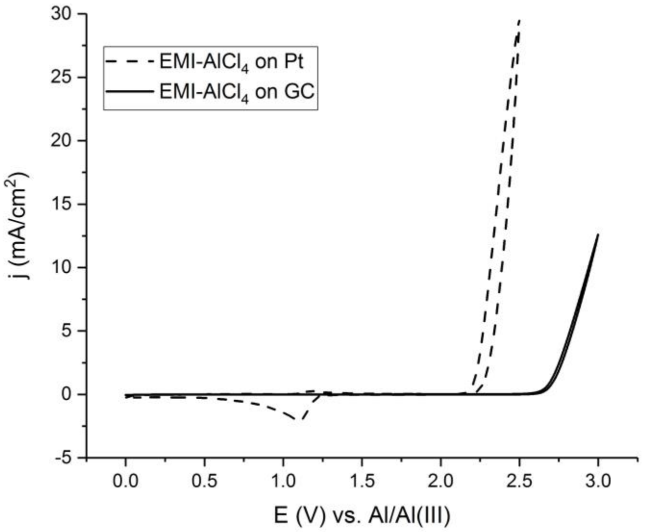
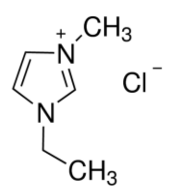


Figure 1 Cyclic voltammograms at 25 mV/s performed in EMI-AlCl$_4$ on platinum and glassy carbon electrodes.

Cyclic voltammetric study of substituted imidazolium-based ionic liquids

As protons are electrochemically active in the system, they presence in aluminate melts is undesirable as their redox activity influences the current efficiency in the battery application. As indirect effect, the moisture content can influence the negative electrode reactions, too. However, getting rid of the moisture is not simple as imidazolium based ionic liquids in particular are extremely hygroscopic. As the presence of water also influences the physicochemical properties (viscosity, conductivity etc.) of the melt, the water content should be known and lowered. Water contents of the acidic melts were determined by Karl-Fischer method inside the glove box for each ionic liquid before electrochemical tests were taken.

As highly active chlorine and AlCl$^-_4$ (could play as a catalyst for substitution) co-exist in the organic system, halogenation on the imidazolium ring, especially at 2nd position, can't be excluded. The liberation of protons during the substitution can be secondary proton source in the system. Beside the EMIC, the following commercially available, substituted imidazolium compounds (with less chance for the halogenation of the ring) have also been tested:



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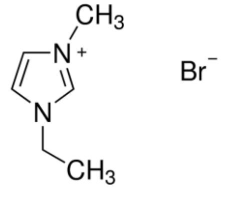

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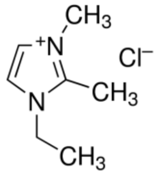

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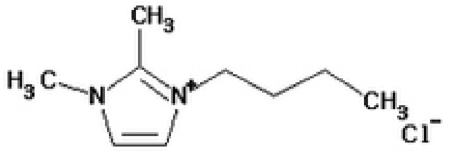


4

1 1-Ethyl-3-methyl-imidazolium chloride (EMIC, ~200 ppm H_2O)

2. 1-Ethyl-3-methyl-imidazolium bromide (EMIBr, <200 ppm H_2O)
3. 1-Ethyl-2,3-dimethyl-imidazolium chloride (123MIC, ~1000 ppm H_2O)
4. 1-Butyl-2,3-dimethyl-imidazolium chloride (BDMIC, ~5000 ppm H_2O)

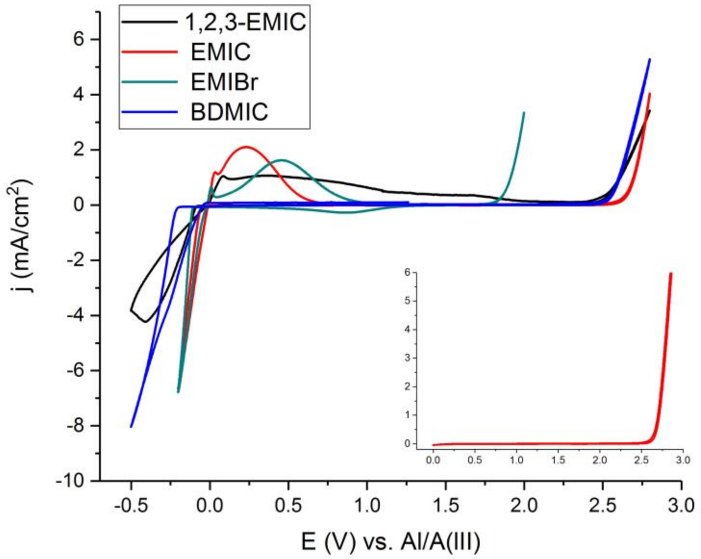


Figure 2 Cyclic voltammograms at 25 mV/s performed in different acidic aluminate melts on glassy carbon electrode.

As it can be seen on Fig 2, the width of the electrochemical potential window is the same in case of various chloroaluminate melts with different imidazolium cations. There is ~100 mV difference in the onset potential of the chlorine evolutions. (Obviously, the onset potential for the bromine evolution is less positive.) No specific electrochemistry can be observed in case of the different cations in the potential range studied. The anodic peak during the aluminum stripping can be observed at different potential and with different peak width, can be connected to the altering water contents in these systems. The higher the water content (more Al-oxide-hydroxide species in the system) the slower the Al stripping from the glassy carbon electrode. As the inset figure shows, the peak does not originate from the electrochemistry of the cation. Comparing the anodic Tafel parameters, the same slopes can be observed in each chloroaluminate. From the point of view of the electrochemical activity of cation, all studied substituted imidazolium compounds can be used as IL component. However, since there is a significant difference in the water contents of different imidazolium chlorides, it is suggested the choose one with less moisture content.

Comparison of the basic electrochemical properties in chloro- and bromoaluminate melts on different substrates

As there are concerns about the reversible chlorine electrochemistry, volatility, and reactivity with the imidazolium ring, basic electrochemical characterization of the less reactive bromoaluminate melt has also been carried out. In case of using bromide-based IL, the expected energy density is lower but a less reactive and the two-phase only (solid/liquid) battery system can be gained in exchange, letting us avoid a toxic gas phase reactant.

During the study comparison has been made between the acidic chloro- and bromoaluminate upon their cyclic voltammetry. Cyclic voltammograms have been checked on both platinum and glassy carbon electrodes (Figure 3). The overpotential for halide oxidation is much lower, the current density is much higher on platinum electrode due to the facile electrode kinetics in both systems compared to values obtained on glassy carbon. Unlike the chloride oxidation, the oxidation of bromide is not irreversible on Pt.

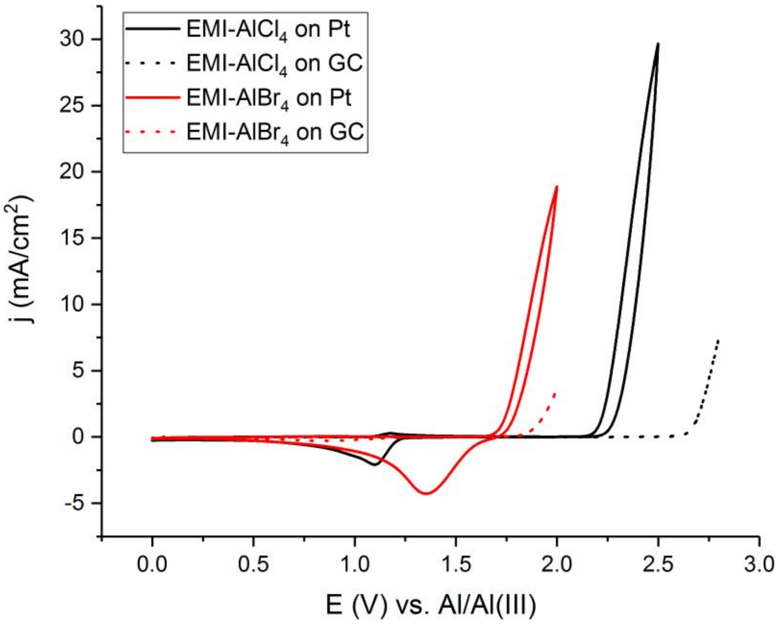


Figure 3 Cyclic voltammograms at 25 mV/s performed in EMI-AlCl$_4$ and EMI-AlBr$_4$ on platinum and glassy carbon electrodes.

Electrochemical study of acidic aluminate melts on different electrode supports

In order to find less precious alternative electrode for the positive electrode reaction, different surface modification techniques and electrode supports have been tried. As it was reported previously Ru, Ti and Co-containing catalysts were found an effective catalyst for Cl_2 reduction reaction in H_2/Cl_2 regenerative fuel cells [cit]. This suggests that they might be promising catalysts for the Cl_2/Br_2 reduction reaction in ionic liquids, as well.

Electrode supports studied are

- carbon-based, with and without Ru modification
    - porous (papers, cloth, sponge etc.)
    - flat (glassy carbon, graphite rod, sheet, pellet etc.)
- metal-based
    - porous (Ti foam, Ni foam)
    - flat (Ru-Ir/Ti sheet).

Detailed list of the electrode supports studied are summarized in Table 1.

Table 1a List of the electrode supports studied in acidic chloroaluminate melt

Substrate	Onset potential for Cl^- oxidation (V)	Comment
BASi Platinum (Pt)	2.05 V	inert
Glassy carbon (GC)	2.65 V	inert
60%Ru@MWNT@GC	2.35 V	dissolution
60%Ru@MWNT pellet	NA	crumbled
Graphite rod	NA	crumbled
Graphite paper	2.0 V	disintegrated
Sigracet carbon paper (SCP)	1.8 V	disintegrated
60%Ru@CP	1.8 V	disintegrated
Carbon cloth (CC)	2.7 V	fringed
60%Ru@CC	2.5 V	fringed
60%Pt@CC	NA	fringed

Table 1b List of the electrode supports studied in acidic bromoaluminate melt

Substrate	Onset potential for Br^- oxidation (V)
BASi Platinum (Pt)	1.70
BASi Glassy carbon (GC)	1.92
Carbon cloth (CC)	1.70
60%Ru@CC	1.70
Graphite rod	1.70
Graphite paper	1.85
60%Ru@GP	1.85
Toray carbon paper (TCP)	1.70
60%Ru@TCP	N/A
Spectracarb paper (SPCP)	1.65
60%Ru@SPCP	1.65
Sigracet carbon paper (SCP)	1.90
60%Ru@SCP	N/A
Freudenberg carbon paper (FCP)	1.70
60%Ru@FCP	N/A
Carbon sponge (CS)	1.80
60%Ru@CS	2.00
Nickel sponge (NS)	1.85

Study of carbon-based supports with/without Ru modification

Different carbon based supports were investigated with and without ruthenium modification in both aluminates. Among the target materials were some commercially available carbon papers with high porosity, various forms of graphite (porous foam, sheet, rod, paper), as well as flat electrodes e.g. graphite sheets, pyrolytic graphite sheets, rods, glassy carbon electrodes (see Table 2). The modification of the electrode was carried out either by chemical vapor deposition of ruthenium or by drop casting Ru-containing ink onto the substrates.

Table 2

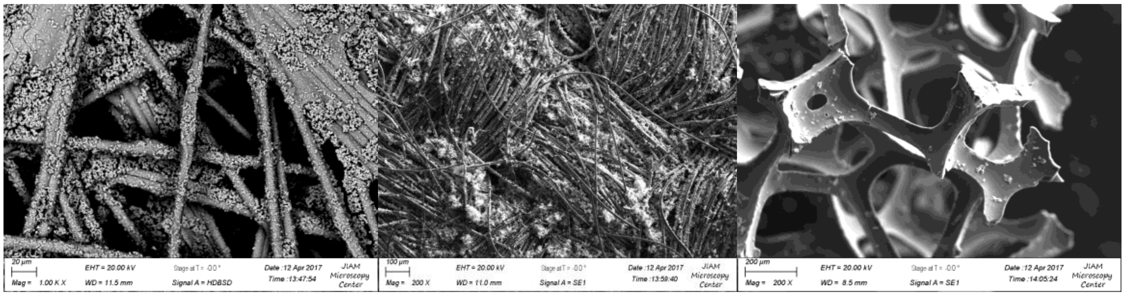
Carbonpaper-based supports:

- Toray® H-090 (w/o Ru)
- Sigracet® 34AA (w/o Ru)
- Spectracarb® 2050A (w/o Ru)
- Freudenberg® F2 (w/o Ru)
- graphite paper (w/o Ru)

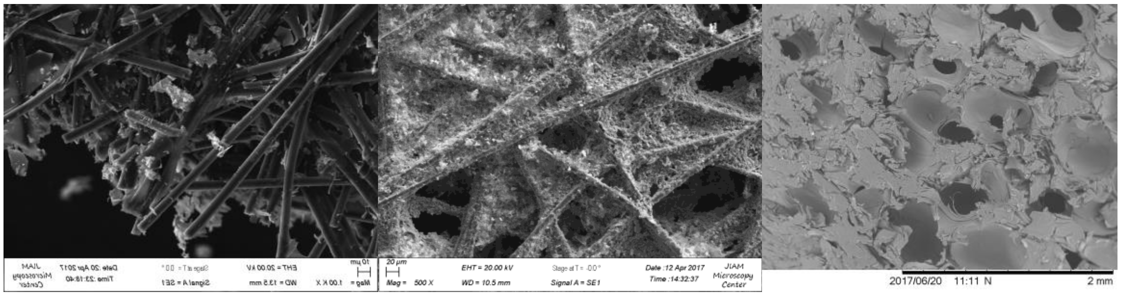
Other carbon-based supports:

- carbon nanotube with Ru (MWNT, 10 nm) (Cheap Tubes)
- carbon sponge (w/o Ru)
- carbon cloth (w/o Ru)
- graphite rod (bare)
- graphite sponge (bare)
- pyrolytic graphite sheet (1mm, w/o carbon black) (K&J Magnetics)

The electrochemical performance has been checked by cyclic voltammetry in case of each bare or modified substrate in both acidic aluminates. Scanning Electron Microscopy (SEM) images were taken from all substrates (see examples on Fig. 4). EDS spectra were also collected prior to and after the electrochemical tests in order to see any changes in the morphology of the substrates and in the catalyst coverage.



Spectracarb paper with Ru **Carbon cloth with Ru** **Carbon sponge with Ru**



Toray carbon paper with Ru **Sigracet carbon paper with Ru** **Bare graphite sponge**

Figure 4 SEM images from some carbon-based electrode materials studied

As it can be concluded from the EDS data, ruthenium was not dissolved from the supports during the tests (Fig. 5).

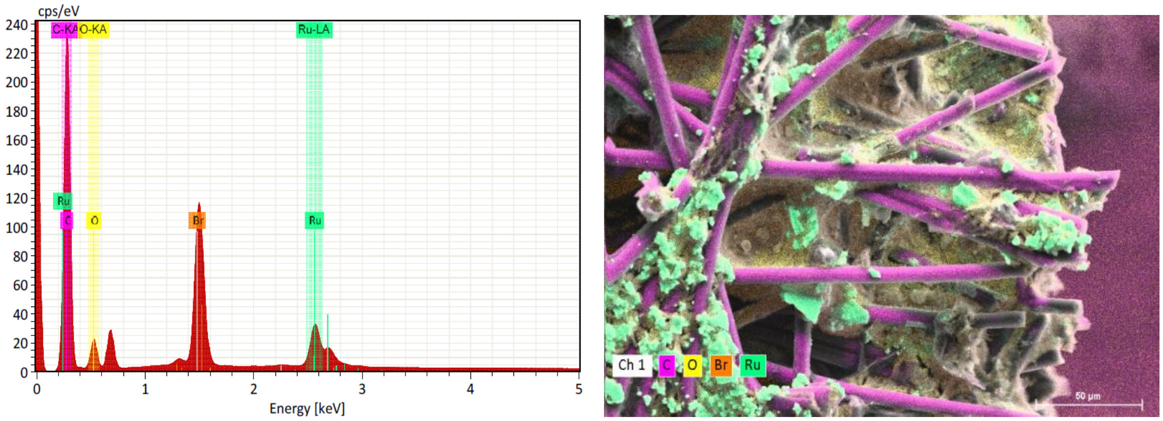


Figure 5 EDS spectra and elemental montage map taken from 60% Ru@Toray carbon paper

Modified multiwalled carbon nanotube (10 nm) slurry containing 60% ruthenium was dropped and dried onto a glassy carbon. As curve shows on Fig. 6a, the chloride oxidation took place at more positive potential by 200 mV on modified glassy carbon in acidic EMI-AlCl$_4$ then that obtained on bare glassy carbon. However, the stability/durability is a critical issue, the activity has been lost during dipping the electrode into IL for a couple of hours. The same durability problem has been concluded from the results in chloroaluminate, when a pellet form of the same catalyst has been tested (disintegration). Other form of the carbon-based substrates also failed either because of short term durability or low performance in the chloroaluminate melt (see Table 1).

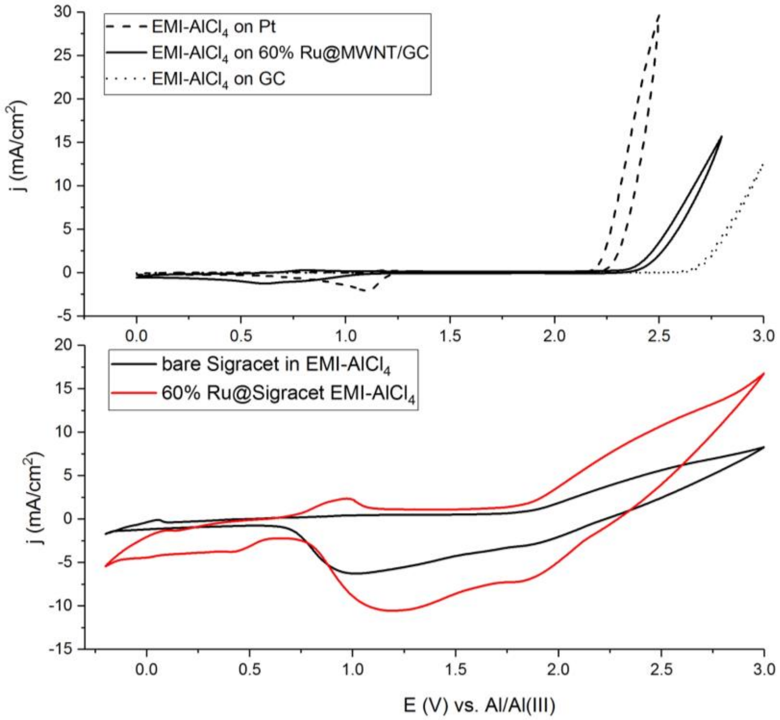


Figure 6 Cyclic voltammograms at 25 mV/s performed in EMI-AlCl$_4$ on different electrodes.
Upper figure (a): CVs obtained at Pt, bare and 60%Ru@ MWNT-modified glassy carbon (GC), lower figure (b): CVs obtained on bare and 60%Ru@Sigracet carbon paper.

Similar catalytic effect was also observed when the Ru catalyst was deposited by CVD onto the on porous carbon paper substrate. Among the porous carbon papers studied, the best performance was obtained with the Ru-modified graphitized Spectracarb paper in bromoaluminate melt. Higher current densities were observed in both aluminates (see Fig.6b, Fig.7a), but the modified carbon paper electrodes were more durable in bromoaluminate melts.

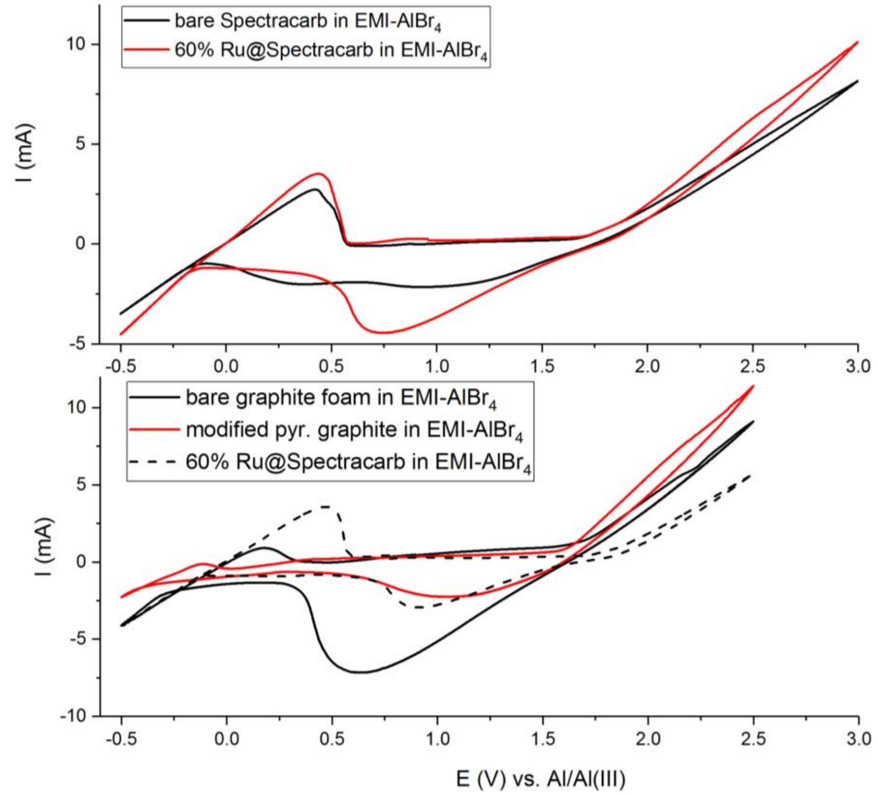


Figure 7 Cyclic voltammograms at 25 mV/s performed in EMI-AlBr$_4$ on the best performed electrodes. Upper figure (a): CVs obtained on bare and 60%Ru@Spectracarb paper, lower figure (b): CVs obtained on bare graphite foam, on graphite powder modified pyrolytic graphite and on 60%Ru@Spectracarb paper.

Among other porous carbon-based supports the graphite-based substrates as

- bare graphite foam,
- porous graphitized paper (e.g. Spectracarb),
- pyrolytic graphite

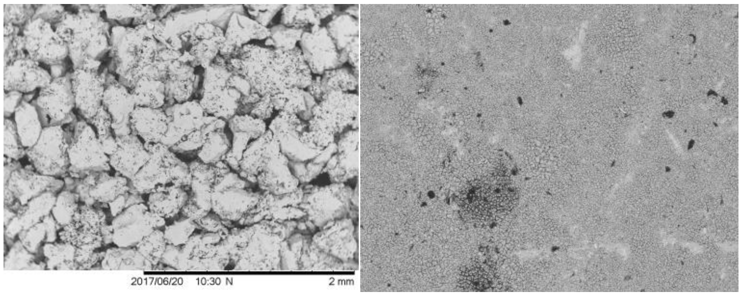
seemed to be the most promising electrode materials in bromoaluminate melts (see Fig. 7b). Significant performance enhancement has been obtained by modification of the pyrolytic graphite surface with pyrolytic graphite powder and carbon black blend in the presence of a specific rubber binder.

Metal-based supports with/without Ru modification

Due to the success of dimensionally stable anodes (DSAs) in the industrial production of chlorine in the chlor-alkali process, Ru and Ti based compounds appear promising as electrode materials for use in a halogen electrode in ionic liquid as well. Bare Ti foam with high porosity and Ru-Ir modified titanium sheet have been tried as candidate anodes (Table 3, Fig. 9).

Table 3

Non-carbon based supports:
• Ti foam (bare, pore size ≤ 100 µm, American Elements)
• Ruthenium-Iridium covered titanium sheet (Ru/Ir 4:1, American Elements)



Bare Ti foam **Ru-Ir on Ti sheet**

Figure 9 SEM images taken from titanium-based electrodes

As the cyclic voltammograms show on Figure 10, the bromide can be oxidized at less positive potential on Ti electrode with high current density than it was measured on the previous carbon-based supports. Under the dynamic voltammetric conditions the $2Br^-/Br_2$ electrochemistry seemed to be irreversible on both electrodes in bromoaluminate, the charging process can't be studied on these electrodes.

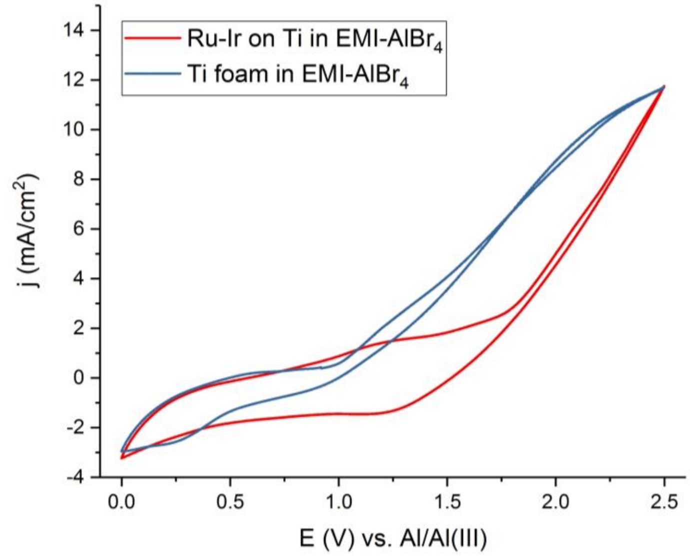


Figure 10 Cyclic voltammograms at 25 mV/s performed in EMI-$AlBr_4$ on bare Ti foam and Ru-Ir on Ti electrode.

Final conclusions

- Most of the electrode materials, carbon supports studied resist to the corrosion in bromoaluminate, no visible disintegration was observed.
- Graphite based supports were found to be the electrodes with the best performance from the electrochemistry of $2Br^-/Br_2$ point of view:
  - graphite sponge
  - pyrolytic graphite sheet
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- Substrates with high surface area, porous supports are favorable
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