On the use of voltammetric methods to determine electrochemical stability limits for lithium battery electrolytes

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Abstract

In previous studies a novel amphiphilic co-polymer was developed for use in lithium-ion batteries. In order to evaluate the electrochemical stability of that electrolyte and compare it with others, a voltammetric method was applied on a set of electrolytes with different salts, solvents and polymers. However, initially the voltammetric methodology was studied. Platinum was found to be the most suited electrode material, experiencing no significant interfering reactions and a proper diffusion-controlled kinetic behaviour when sweep rate was varied. Furthermore, the influence on the voltammograms of adding water traces to the electrolytes was studied. It could be established that the oxidation peak around 3.8 V versus Li was related to water reactions. It was concluded that quantitative voltage values of the stability limits were difficult to assess using voltammetry. On the other hand, the method seemed well suited for comparison of electrolytes and to investigate the influences of electrolyte components on the stability. The voltammetric results varied little between the different electrolytes evaluated and the anodic and cathodic limits, as defined here, were in the range of 1 and 4.5 V vs. Li, respectively. Although the novel polymer did not affect the stability limit significantly it seemed to promote the breakdown reaction rate in all electrolytes tested. Furthermore, the use of LiTFSI salt reduced the stability window.
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Keywords: Lithium-ion battery; Electrolyte; Electrochemical stability; Cyclic voltammetry

1. Introduction

Rechargeable lithium-ion batteries, commercially launched by Sony in the beginning of the 1990s, are still being developed in terms of new electrode materials and electrolytes. An obvious goal is to improve performance, but safety aspects are generally ascribed a high priority since these batteries have rather reactive electrodes compared to other batteries. An important safety aspect is the use of stable electrolytes. If the stability limit of the electrolyte is violated it will start to decompose. This may eventually cause cell failure, or possibly gas evolution, that may be rapid at higher temperatures presenting a safety hazard. In the Swedish research program "Batteries and fuel cells for a better environment" one research field was to study novel polymer gel electrolytes with improved performance compared to traditional gel electrolytes for lithium-ion batteries [1,2]. Several electrolytes were evaluated, using different polymers, solvents and salts. A conductivity-optimised electrolyte based on a novel amphiphilic co-polymer

denoted by FA77EO9, was realised. An amphiphilic polymer was chosen to achieve a selective surface chemistry, possibly improving the electrochemical properties, such as electrochemical stability and charge transfer resistance, at the electrode surfaces in a battery. The influence of using a polymer in the electrolyte on the charge transfer was investigated in a different study [3]. The present study deals with the influence of different electrolyte components on the electrochemical stability of the electrolyte.

In order to study the electrochemical stability limits of electrolytes, i.e. the potential where electrolyte oxidation and reduction start to occur, voltammetric methods are generally employed. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) are two common voltammetric methods. Other methods have been proposed [4–6], however, no significant advantage has been demonstrated. Cycling real lithium-ion cells with the electrolyte of interest has also been used to assess the stability of electrolytes. However, that method suffers from the difficulty in separating electrode related effects from electrolyte breakdown. It is also time consuming. If cycling is to be used for stability studies the cycling limits should be varied and the quota between charge and discharge capacity should be studied. However, varying cycling limits may be difficult with common lithium-ion

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electrode materials because they have a limited operating voltage. Thus, the ease, the well developed theory [7,8] and the usually rapid experiments of the voltammetric methods make these methods preferential.

Voltammetric methods also suffer from drawbacks. Electrode materials that do not experience the regular charge/discharge reactions of the battery must be used. Otherwise the charge/discharge reactions would simply dominate the voltammetric response. In a related research field, that of organic electrochemistry, it is widely known that the electrochemical reaction products and reaction paths vary significantly with the use of different electrolytes and with different electrodes. It is accepted that all experimental parameters affects the reactions occurring, and little is known about how this occurs. This fact has also been observed in the field of electrolyte stability [9]. Hence, voltammetric methods may be difficult to use as a tool to quantitatively probe and predict the electrochemical stability of an electrolyte in a lithium-ion cell, because the electrodes are different. This implies that the breakdown reactions probed using voltammetry might be different from those in real cells. A possible way of overcoming this problem is to choose electrodes that result in the most limited stability window, i.e. the most reactive or catalytic electrodes, resulting in a result close to the thermodynamic stability window of the electrolyte. Then, it seems reasonable to assume that the voltammetric results, in terms of stability limits, should be applicable to real batteries.

Previously, several electrode materials have been evaluated for voltammetric probing of electrolyte stability, however, difficulties have been observed with many of them. Problems that may interfere with the measurements include electrode corrosion at high potentials, observed with for example Ni electrodes [10], and Li-plating/alloying/insertion at low potentials appearing for many electrode materials [10–12]. Graphite electrodes, together with other types of carbon electrodes, such as glassy carbon (GC) [13,14] and vitreous carbon [11], have been used, since they do not suffer from corrosion. However, they experience Li-insertion. Stainless steel (SS) has been widely used [15–22], although it is known to have a corrosion resistance limited to a certain potential window [23] and has a complex surface chemistry. To further clarify the matter of a suitable highly catalytic electrode material, that do not suffer from interfering reactions, a study of different electrode materials seems to be in place.

Although quantitative stability limits probed using voltammetry may be somewhat uncertain, the methodology should enable investigations of the influence of the different components of an electrolyte on the stability. It should thus suit as a screening method for finding novel electrolytes with improved stability. Influences of salt [15,16,24], solvent [10,11,13,14,16] and polymer [16] on the stability window have been examined previously using voltammetry. Thus, it seems interesting to employ voltammetry as a qualitative tool to examine the stability limits of the novel

electrolytes compared with other electrolytes and study the influences of varying salt, solvent and polymer.

In this study, a voltammetric method using a suitable electrode material was developed and used to study a set of different electrolytes, including a novel gel electrolyte. First, different electrode materials were evaluated. For the most promising materials the nature of the occurring reactions was studied by varying the sweep rate. Furthermore, the influence of water impurities on the voltammograms using the chosen electrode was investigated for various electrolytes. Finally, to demonstrate the abilities of the method, a set of electrolytes, with varying salt, solvent and the presence, as well as type of polymer, was probed using the developed voltammetric method.

2. Experimental

2.1. Electrolyte preparation

The electrolytes were prepared, handled and characterised in an argon filled glove box ($H_2O < 1$ ppm, $O_2 < 20$ ppm), where also all the chemicals were stored. Lithium hexafluorophosphate, $LiPF_6$ (Merck, Selectipur), was vacuum dried at $80\,^{\circ}C$ for 24 h. Lithium bis(trifluoromethanesulfon) imide, LiTFSI (3 M, Battery grade), was used as received. The solvents (Merck, Selectipur), ethylene carbonate (EC) and butyrolactone (gBL), with certified water levels below 20 ppm, were stored over molecular sieves to ensure the purity. The polymers used were dried under vacuum ($p < 10^{-5}$ bar) for 48 h before use to remove water contaminations. The conductivity optimised amphiphilic graft copolymer (FA77EO9) depicted in Fig. 1, synthesised and characterised previously [1,2], was determined to contain 76 wt.% of the fluorinated block (a) and 24 wt.% of the ether block (b). For details about the preparation and characterisation of the polymer see [1,2]. The molecular weights (M_n) of FA77EO9 and PMMA were 48,000 and 40,000 g/mol, respectively, as determined by gel permeation chromatography. First the solvents were prepared, EC:gBL 2:1 (by volume) and pure gBL. Then salt was added to obtain 1 M electrolytes. Finally, for the polymer containing electrolyte samples, 30 wt.% polymer was added to the solution, resulting in a viscous liquid electrolyte after some time. FA77EO9 dissolved/swelled readily (approximately 12 h) in the
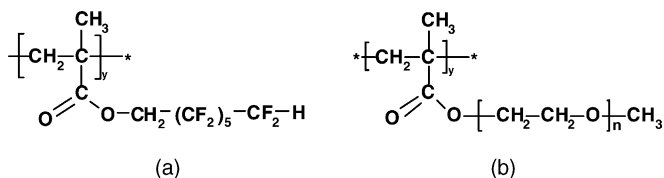

Fig. 1. The novel conductivity optimised polymer FA77EO9 consisted of 76 wt.% of the fluorocarbon monomer (a), and 24 wt.% of PEO macromonomer (b).

electrolyte solutions while the electrolytes based on PMMA presented a slow dissolution/swelling processes (1 week). Heating was avoided due to the risk of degradation. A total of 12 different electrolytes were prepared in this way, with all combinations of salts (LiPF$_6$/LiTFSI), solvents (gBL/EC-gBL) and with/without addition of polymers (PMMA/FA77EO9).

2.2. Preparation of electrode materials

Working electrodes of platinum (Pt), stainless steel (SS) (Sandvik 1305R), nickel (Ni), glassy carbon (GC) and porous (8% porosity) graphite plates were evaluated. All metal foils were cleaned with acetonitrile (Merck, HPLC-grade) and dried carefully. Possible surface impurities of the Pt and Ni foils were mechanically removed prior to use each time, and then they were cleaned. The graphite plates, cut from a rod (Ellor +25, Carbone Lorraine), were polished and dried (175 °C 12 h, vacuum ($p < 10^{-5}$ bar) 12 h) before use. The SS and graphite electrodes were used only once. The GC was held at 3 V versus Li for sufficient time to de-intercalate all lithium after each experiment, cleaned with acetonitrile and dried.

2.3. Voltammetry

A three-electrode cell, made of Teflon^{TM}, with lithium counter and reference electrodes, was used for the voltammetry measurements. The reference electrode was situated close (<1 mm) to the working electrode. The working electrode area was limited to a geometric area of 0.5 cm^2 by a Teflon ring, for all electrodes except the GC, which had a surface of 0.25 cm^2. LSV was performed with a computer controlled Solartron$^®$ 1287 Electrochemical Interface, employing the Corrware^{TM} software. Most experiments were carried out at a sweep rate of 5 mV/s, sampling data once each second, between open circuit potential (OCP) and 6 V versus Li for the anodic sweeps, and OCP and −0.1 V for the cathodic sweeps. For some experiments the sweep rate was altered. All experiments were performed at 25 °C in the glove box.

3. Results and discussion

3.1. Electrode material

In order to find a suitable electrode material for probing electrolyte stability limits Pt, SS, Ni, GC and graphite were tested as electrode materials, using the electrolyte gBL/LiPF$_6$. Nickel was not evaluated in the anodic region due to its known corrosion problems [10]. Studying the anodic sweeps displayed in Fig. 2, it can be observed that all samples experienced a "background" current, caused by non-Faradaic processes, e.g. double layer charging. Such currents increase with sweep rate, hence a low sweep rate,
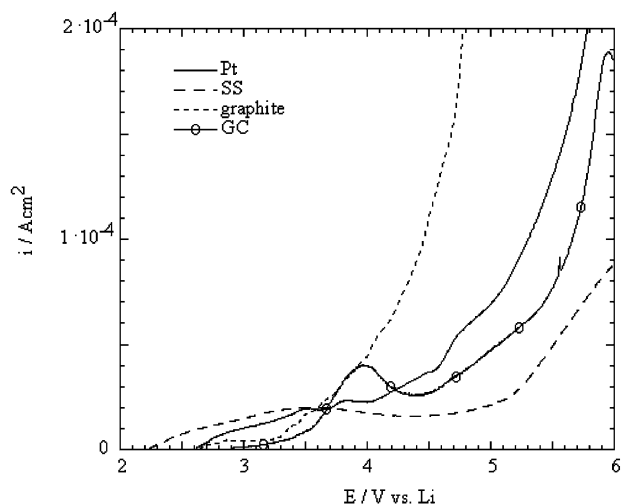

Fig. 2. Anodic voltammograms (OCP to 6 V vs. Li) for different electrode materials in gBL/LiPF$_6$, as indicated in the figure. The sweep rate was 5 mV/s, and the temperature 25 °C.

e.g. 0.1 mV/s, has been used in some previous studies. However, as long as these currents do not dominate the results, the use of such low sweep rates only makes the experiments unnecessary tedious and time consuming. The influences of these background currents has been treated more extensively in other work [25].

The results in Fig. 2 clearly demonstrate that the electrode material used influences the results. As explained in the introduction, a suitable electrode material should experience rapid electrode kinetics, in this case resulting in a high current density at a certain potential. In Fig. 2, it can be seen that the porous graphite electrode experienced the highest geometric current density in the whole potential region. However, this is an effect of the large surface area rather than rapid kinetics. A problem when using that electrode was to perform repeatable measurements. The wetted surface area was difficult to control and measure; hence, the porous graphite electrode was considered improper. Of the remaining materials, Pt resulted in the largest current densities, indicating its suitability for stability measurements. In contrast the stainless steel electrode experienced the lowest currents.

It was difficult to determine at which voltage breakdown reactions of the electrolyte started to occur. To compare the results it seemed proper to define a stability limit in terms of a current density. In this study, the stability limit was defined to be the potential where a current density of 50 μA/cm^2 was reached. If a stability limit would be defined on required battery shelf life (e.g. self discharge in 1 month) or lifetime (e.g. decomposition of 20 μm electrolyte in 2 years), the limit in terms of current density would be significantly lower, in the range of a few μA/cm^2 and pA/cm^2, respectively. However, to monitor current densities at pA/cm^2 great effort would be necessary to reduce the background signals below such levels. The limit defined here is merely used as a tool to

compare the results rather than a strict reaction rate limit. As can be seen in Fig. 2, above that limit, the current density increased very dramatically for all materials. From that definition, the oxidation stability limit of the electrolyte studied could be determined for the different electrodes used. It was 4.7 V using Pt, 5.1 V for GC and 5.5 V for SS. Again, the differences probably reflect the varying kinetics of the electrodes. The thermodynamic stability limit of the electrolyte should be independent of electrode material. The results indicate that the limit should be somewhere just below 4.7 V versus Li. A speculative explanation for the delay of oxidation currents on SS until above 5.2 V is the breakdown of the passivation layer of the SS, that might appear at around these potentials [23]. If so, SS is inappropriate because of the dominant effect of the passivation processes of the material. However, further investigations are necessary to clarify this matter. The response of the GC electrode was somewhat confusing, with a peak before the high voltage onset. Such a peak may appear due to surface reactions, or due to reactions with a species in the solution that is strongly hindered by mass transport. This indicates that the peak corresponds to some interfering reaction, making the material less suited for stability studies. From the results in the anodic region Pt seem to be the most suitable candidate for probing the oxidation stability limit, having rapid kinetics and no interfering reactions.

In the cathodic region, i.e. at low voltages, reduction breakdown reactions of the electrolyte are of interest. Interfering currents from lithium plating, under potential deposition (UPD), alloying or insertion might also occur together with surface reactions of the electrode material itself and non-Faradaic processes. The voltammograms achieved for Pt, Ni, SS, GC and graphite presented in Fig. 3, recorded with gBL/LiPF$_6$ electrolyte, showed some of these
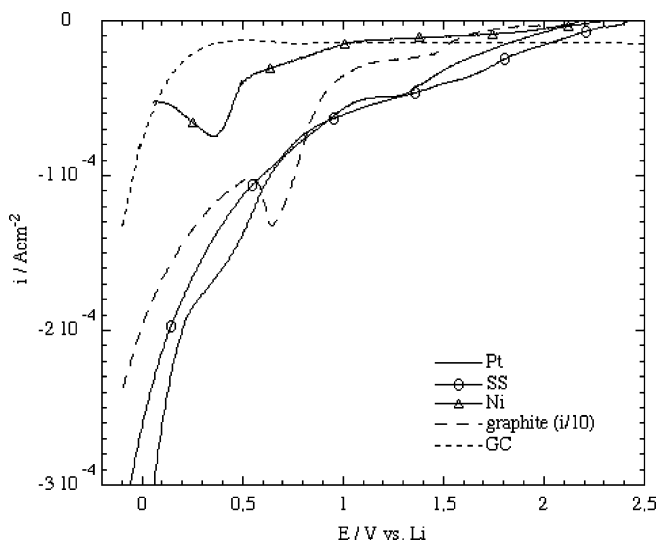

Fig. 3. Cathodic voltammograms (OCP to −0.1 V vs. Li) for different electrode materials in gBL/LiPF$_6$, as indicated in the figure for graphite *i*/10 is displayed. Sweep rates were 5 mV/s, and temperature 25 °C.

problems. For Ni and graphite a reduction peak was observed around 0.5 V. Similarly, a very weak peak was also present for Pt around that voltage. Reduction peaks in this region has previously been attributed to both Li-UPD [10,12,26] and the formation of a solid electrolyte interface (SEI). The nature of the reactions occurring at low potentials in this type of electrolytes is a research field in its own and is not dealt with further here. Comparing the magnitudes of the reduction currents, the graphite resulted in the largest current density, due to its porous nature. GC and Ni resulted in the smallest responses, due to slow kinetics, making these materials inappropriate. The remaining materials Pt and SS yielded similar current signals. If the previous definition of stability is employed the reduction stability limit of the electrolyte becomes 1.2 V for both SS and Pt. This stability limit is in line with recent results for similar electrolytes [27]. At voltages below 0.5 V interfering reactions related to Li plating, deposition or alloying seem to be present for all materials tested. From the cathodic results both Pt and SS seem interesting.

To further investigate the suitability of the electrodes the nature of the occurring reactions was studied by varying the sweep rate. Rigorous theories of the influence of sweep rate on CV for different reaction types are available [7,28]. Two categories of reactions can be identified; diffusion controlled and surface related reactions. For reactions involving species present in the electrolyte, reacting at the electrode, diffusion of a reagent or product in the electrolyte phase is inevitable. For this type of reaction the peak current should be proportional to the square root of the sweep rate, even for quite complex reaction schemes involving several steps. Reactions without a diffusion step, i.e. where both reagents and products remain at the surface, e.g. oxidation of a metal surface to form metal oxides, should be proportional to the sweep rate. Electrolyte decomposition reactions typically involves irreversible mechanisms [5] that should be diffusion controlled. This means that an electrode suitable for electrolyte breakdown measurements should show a square root relation between breakdown current and sweep rate. Sweep rate analysis was employed for Pt, SS and graphite electrodes with gBL/LiPF$_6$ electrolyte. Both 25 and 1 mV/s were evaluated and the results compared with those achieved at 5 mV/s. Fig. 4a–c presents anodic and cathodic sweeps for Pt and SS recorded for the different sweep rates. For the Pt electrode, a square root relation between current and sweep rate seem to be valid in both the anodic and cathodic regions. Although there is a small discrepancy in the cathodic region, this indicates that the current is dominated by a true electrolyte breakdown reaction, involving diffusion of some specie. For the SS electrode on the other hand the situation seem to be more complex. In both the anodic and cathodic regions neither relation seem to fit. This could be the result of a situation where different types of reactions take place. A combination of electrode surface reactions and electrolyte reactions could cause such responses. The sweep rate analysis indicates that Pt is the most suitable material for
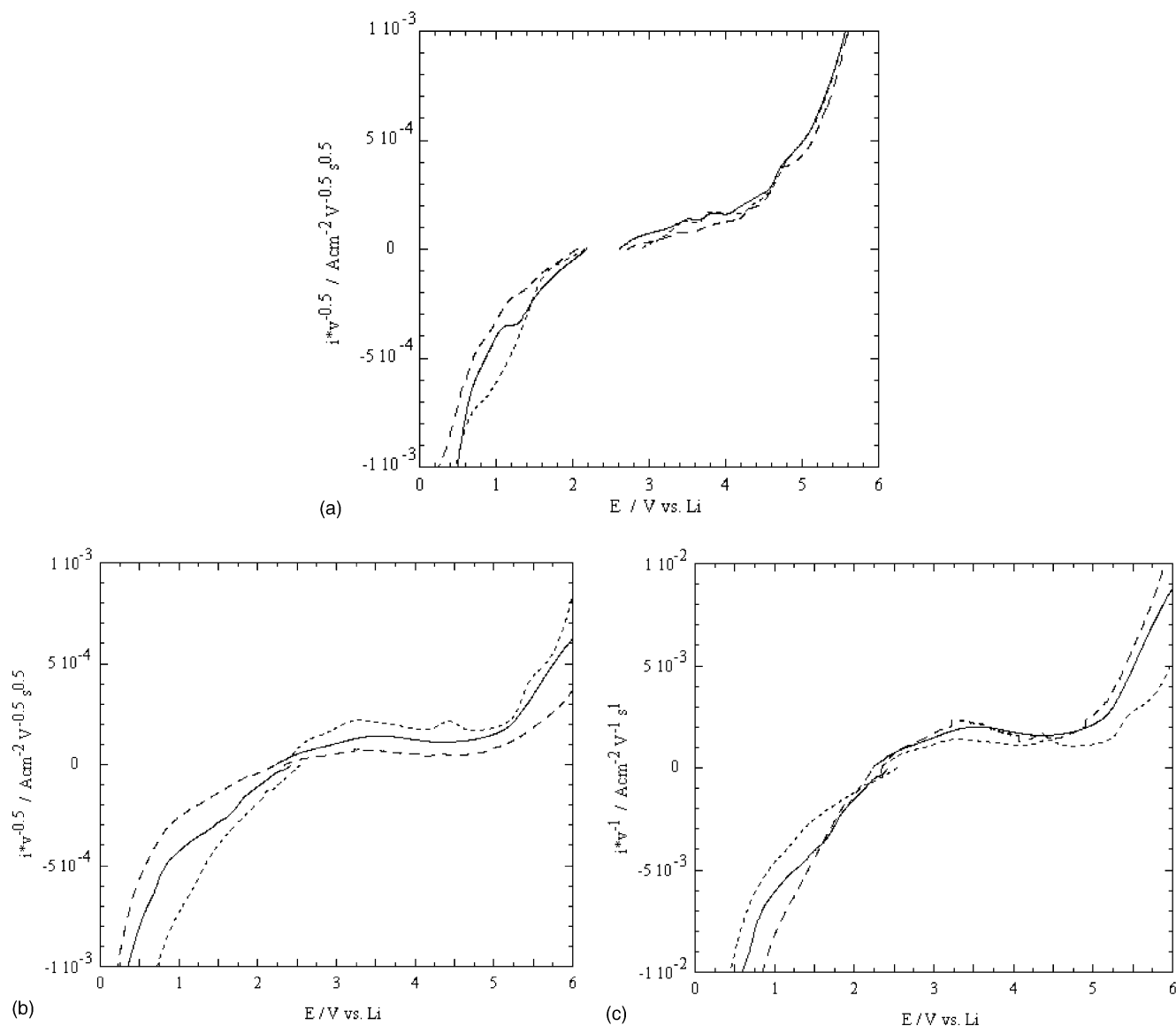
Fig. 4. (a) Anodic and cathodic sweeps, normalised with square root of sweep rate, for Pt in gBL/LiPF$_6$ obtained at different sweep rates: 5 mV/s (—), 1 mV/s (– – –) and 25 mV/s (- - -). (b) Anodic and cathodic sweeps, normalised with square root of sweep rate, for SS in gBL/LiPF$_6$ obtained at different sweep rates: 5 mV/s (—); 1 mV/s (– – –) and 25 mV/s (- - -). (c) Anodic and cathodic sweeps, normalised with sweep rate, for SS in gBL/LiPF$_6$ obtained at different sweep rates: 5 mV/s (—); 1 mV/s (– – –) and 25 mV/s (- - -).

electrolyte stability measurements, and that SS should be used with care due to the presence of surface related currents, employing lower sweep rates (<1 mV/s) to reduce the signals from electrode surface reactions.

3.2. Influence of moisture contamination

In many papers the importance of using dry chemicals for the electrolyte is mentioned, especially when studying electrochemical stability [10,12,19]. Usually, the water content is analysed using methods such as Karl–Fischer titration. Few studies of the influence of water impurities on voltammograms have been found [29], although the method has been proposed by others [30] for quantitative water trace content

analyses. To study how water traces affected the voltammograms, i.e. identify the peaks related to moisture contaminations all samples were subjected to controlled addition of water traces. LSV was performed using Pt electrodes for the samples with and without added water. Reactions that one might look for when adding water are [12], oxygen evolution (oxidation) in acidic solution, with a standard potential (E^0) of 4.28 V versus Li, and the reduction of protons to hydrogen gas, E^0 at 3.05 V. As can be seen in Fig. 5 the addition of 100 ppm water to gBL/LiPF$_6$ increased the response in the whole anodic region, with a specific peak increasing at around 3.8 V. This indicates that the peak is related to water reactions, possibly oxygen evolution. When only 10 ppm water was added, the increase in anodic current in the whole
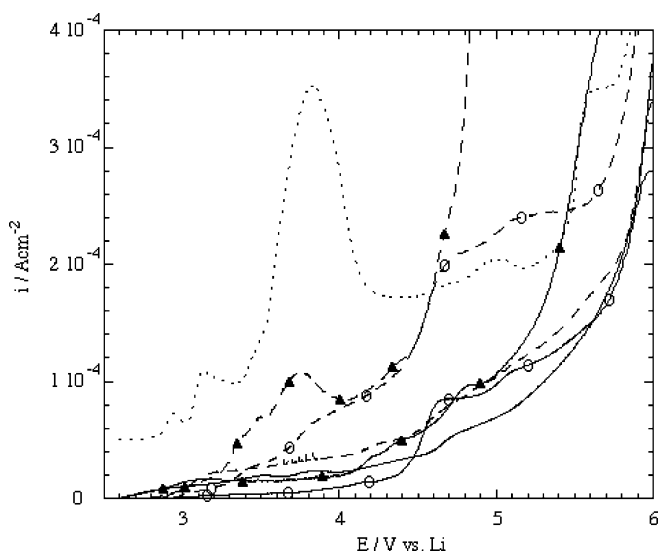
Fig. 5. Anodic sweeps at 5 mV/s for three different electrolytes with and without addition of water traces. The following results are displayed: gBL/LiPF$_6$ (—), with 10 ppm (- - -) and 100 ppm (· · ·) water added; PMMA/gBL/LiPF$_6$ (–○–) with 10 ppm water (- -○- -); and FA77EO9/gBL/LiPF6 (–▲–) with 10 ppm water (- -▲- -).

Fig. 6. Anodic sweeps on Pt at 5 mV/s displaying the influence of the electrolyte salt. Results for gBL/LiPF$_6$ (—), EC-gBL/LiPF$_6$ (–○–), gBL/LiTFSI (- - -) and EC-gBL/LiTFSI (- -○- -) are represented.

region, and at 3.8 V, was small compared with the signal from the pure sample. Additionally, the observations indicated that the level of water contamination in the original sample electrolyte was well below 100 ppm, and rather in the range of 10 ppm. This procedure was repeated for all the used electrolytes, and the same conclusion could be drawn for all samples. Possibly, the method may be used to estimate the level of water, and other, impurities in electrolyte samples.

An interesting feature could be noticed when comparing the effect of adding water to the different electrolytes. Addition of 10 ppm water to the polymer containing electrolytes resulted in the largest change in current response, the effect being most pronounced for the electrolytes based on FA77EO9. Thus, both the PMMA-based and the novel FA77EO9-based electrolyte experienced an increased water sensitivity compared to their liquid counterparts.

3.3. Comparing electrolytes

The method of adding or varying components in the electrolyte and comparing the resulting voltammograms can be applied to investigate the effect of using different solvents, salts and polymers. This possibility will be explored in the following section. Voltammograms were recorded for a variety of electrolytes, both anodically and cathodically, using a Pt working electrode and a sweep rate of 5 mV/s. In order to study the influences of solvent, salt and polymer, these parameters were all varied. The results were compared and the significant effects will be pointed out below. No clear difference could be detected between the two solvent systems used, gBL and EC-gBL. The salt, on the other hand,
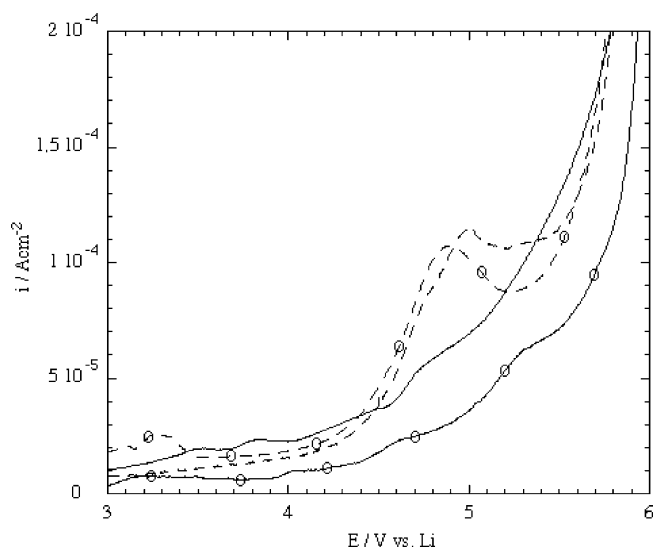
displayed an influence in terms of stability. In Fig. 6, anodic results for different electrolytes without polymer are compared. It can be observed that the electrolytes based on the LiTFSI salt presented a different behaviour than those based on LiPF$_6$. The LiTFSI salt seems to have an increased sensitivity towards oxidation compared to LiPF$_6$. A limited stability of the TFSI-anion has also been observed previously [14,20].

When polymer was added to the electrolytes, other trends could also be observed in the voltammograms. As can be seen in Fig. 7a, where anodic sweeps for electrolytes based on EC-gBL/LiPF$_6$ are plotted, the sample with FA77EO9 resulted in the highest oxidation currents above 5 V. However, following the previous stability definition of 50 μA/cm^2, most electrolytes showed roughly similar stability limit of around 4.5 V. This could mean that the polymer FA77EO9 promotes the oxidation rate in some way, without significantly changing the potential where oxidation starts, i.e. the thermodynamics. In a different study [31] cycling results for LiMn$_2$O$_4$ (3.3–4.2 V versus Li) with various electrolytes were analysed and it was found that the ratio Q_{ox}/Q_{red} increased when FA77EO9 was added, without affecting cycling capacity significantly. That result supports the proposed oxidation rate promotion of the FA77EO9. In contrast to FA77EO9, the addition of PMMA seems to reduce the oxidation rate to some extent, as concluded from the observed current plateau between 4.6 and 5 V. This may have been caused by a reduced mass transport in these electrolytes, also reflected by the higher viscosities they experienced. Another plausible explanation of the behaviour is the formation of a polymer rich layer on the surface of the electrode. This would reduce the oxidation rate by shielding parts of the surface or by causing slower transport to/from the surface of the reactants. However, in a recent study [3]
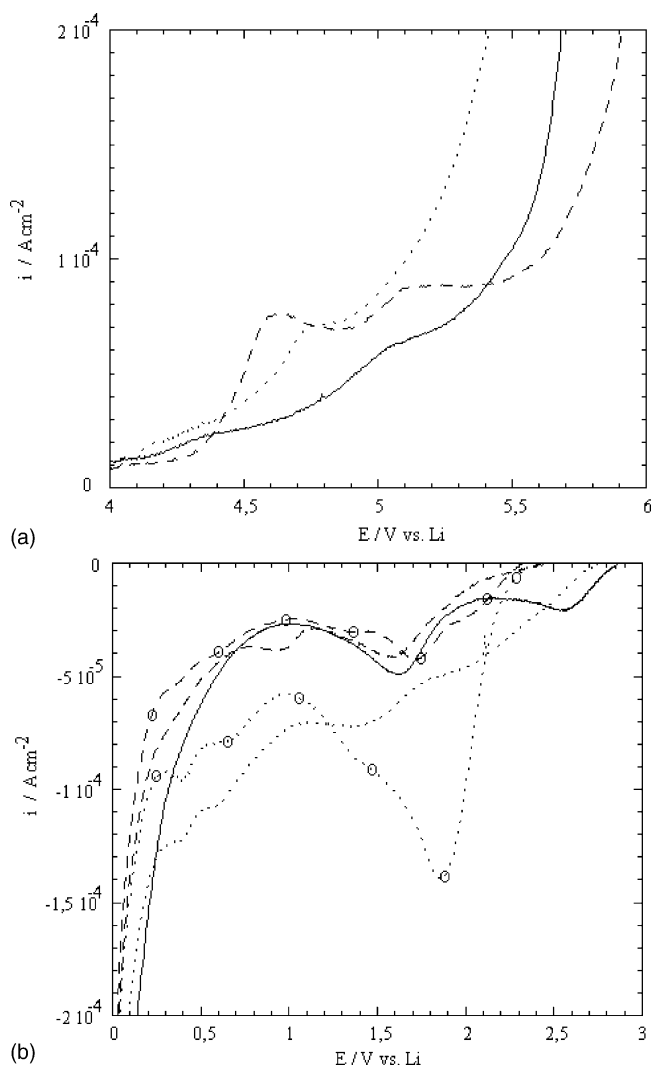
Fig. 7. (a) Anodic sweeps for different electrolytes showing the influence of polymer. Electrolytes based on EC-gBL/LiPF$_6$ with: no polymer (—), PMMA (– – –) and FA77EO9 (- - -) are displayed. (b) Cathodic sweeps for different electrolytes showing the influences of polymer and salt. The displayed electrolytes are: EC-gBL/LiPF$_6$ (—), PMMA/EC-gBL/LiPF$_6$ (– – –), PMMA/EC-gBL/LiTFSI (–○–), FA77EO9/EC-gBL/LiPF$_6$ (- - -) and FA77EO9/EC-gBL/LiTFSI (- -○- -).

containing FA77EO9 indicated that the polymer enhanced the water oxidation reaction. Hence, it is possible that the presence of both LiTFSI and FA77EO9 strongly promotes the reactions with water and/or oxygen residues also in the cathodic region, explaining the observed peak.

In Fig. 7b, another interesting result can be observed. The influence of polymer on the reaction rate is similar to that in the anodic region. Again, PMMA seems to reduce the reduction rates, whereas the FA77EO9 increases these rates. It is difficult to conclude the reason for this behaviour based on this study. However, it is clear that the addition of polymer influences the reaction rate rather than the stability of the electrolytes studied. Applying the stability limit previously defined to the cathodic sweeps results in an unreasonably wide variation in the stability limit, from 2 to 0.5 V. This demonstrates the drawbacks of using a stability limit definition in terms of a current density. If one instead studies the potential where the main reduction starts, i.e. where the current starts to increase rapidly, it can be seen that most electrolytes have onsets around 1 V. This stability limit would correspond well with that reported recently by Zhang et al. for several electrolyte solvents, and is probably close to the true thermodynamic limit.

4. Conclusions

In this study, the importance of using a suitable electrode material when studying the electrochemical stability limits of electrolytes using a voltammetric method was demonstrated. Furthermore, the abilities of voltammetry, in terms of detecting stability limits of different electrolytes and to probe influence of moisture contamination, were evaluated.

The most versatile electrode for probing the electrolyte stability prove to be platinum both in the anodic and the cathodic regions. It experienced rapid reaction kinetics with reactions behaving like electrolyte breakdown reactions would and presented no significant interfering reactions. It was shown that a general definition of stability limits in terms of onset current density is problematic to achieve due to influences from the electrode material and the used sweep rate. Nevertheless, if suitable electrodes are used and sweep-rate is kept constant, the voltammetric methods serves as a qualitative tool when studying stability limits rather then a quantitative. Thus, it is suitable for comparing electrolytes and the influences of electrolyte components, additives and impurities.

The moisture addition method yielded interesting results. It provided information on which peaks were related to water reactions. Furthermore, the moisture sensitivity of the electrolyte could be studied. The electrolytes based on the FA77EO9 seemed to be most sensitive to water traces.

Different electrolytes were also studied in terms of stability limits. Although quite different electrolytes were studied, the differences in the voltammograms were minor. No significant effect could be related to the choice of solvent.

no effect in terms of Li-insertion kinetics could be observed when adding 24 wt.% PMMA to a similar electrolyte. Thus, the latter proposed mechanism may be faulty. Clearly, the two different polymers tested differ in the effect on the oxidation rate.

The different electrolytes were also compared in the cathodic region. As can be seen in Fig. 7b, the combination of LiTFSI and FA77EO9 produced a reduction peak around 1.5–2 V, which was not present for the other electrolytes. Previously, peaks in this region has been ascribed to reduction of water or oxygen impurities [26]. If these impurities had been present in the base chemicals the peak should then have been present for some of the other electrolytes as well. However, the result of adding water traces to electrolytes

However, the LiTFSI salt experienced a limited stability window. Furthermore, a breakdown rate promoting effect could be detected when the FA77EO9 polymer was added, both in the anodic and cathodic region. In contrast addition of PMMA seemed to reduce the reaction rate.

This study may have clarified some aspects of the use of voltammetry for electrolyte stability investigations, and possibly contributed to the development of the methodology, but is far from complete. Further investigations into the area maybe in combination with other techniques, detecting the chemical species present, are necessary to increase the knowledge in this field.

Acknowledgements

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