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Behaviour of PEO-urethane in solutions of carbonates. Synthesis and electrochemical characterisation of PEO-urethane–coke electrodes

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We studied the behaviour of PEO-urethane, resulting from a polycondensation *in situ* of PEO [poly(ethylene oxide)] with urethane, towards organic carbonate electrolytes. We analysed the weight increase of the PEO-urethane with propylene carbonate (PC) or dimethyl carbonate (DMC) and a lithium salt at different concentrations at different times. Results indicate that the diffusion of the carbonate electrolyte is clearly controlled by the PEO-urethane–lithium salt interactions with PC based solutions and by the PEO-urethane–$LiAsF_6$. $(DMC)_2$ interactions with DMC based solutions.

Comparing the transport properties of PEO-urethane with that of Celgard in a liquid electrolyte confirms the results for the weight increase as they suggest a preferential solvation of lithium species by the PEO-urethane network with PC and by DMC when the latter solvent is used.

Composite electrodes containing coke and PEO-urethane were prepared using chemical *in situ* curing. The dependence of the electrical properties of these composites on the coke content was studied. We found an electrical percolation weight loading close to 46%. The influence of the PEO-urethane on the electrochemical behavior of coke was also studied in a carbonate electrolyte using these composite electrodes. A passivation phenomenon always occurs with the first reduction but the stability of the lithiated coke is reduced little with the PEO-urethane.

There has been considerable research to develop lithium ion rechargeable batteries based on a carbon (coke or graphite) anode and a transition metal oxide cathode.[1–8] Carbon has cycling faradic efficiencies close to 99%, which is suitable for an industrial application in batteries. It has been demonstrated that the lithium insertion into the carbon matrix is accompanied, as already reported for metallic lithium, by the formation of a surface passivating layer built up by some reduction products of the electrolyte.[9,10] This layer strongly influences the stability of the lithiated carbon toward the electrolyte. We have already reported,[11,12] that the passivating layer dissolves in an organic electrolyte based on carbonate solvents so that it does not fully protect the lithiated carbon from reactions with the electrolyte. This generates a capacity loss and self discharge phenomena between anode and cathode.

To overcome these difficulties, much effort has been devoted to improving the stability of the passivating layer by modifying the nature of the electrolyte. In this context, use of dry polymer electrolytes appeared beneficial since they should lower solubilities of species and limit their migration, *via* the electrolyte, between the electrodes. However, their low conductivities preclude industrial use and recent research has been targeted toward hybrid electrolytes, *i.e.* a polymer matrix swollen with a liquid electrolyte.[13–15] Many hybrid electrolytes reported in the literature exhibit high ionic conductivities but also deficiencies such as poor mechanical properties so that they often have to be hardened by chemical or physical curing.[15] A few years ago, Cheradame *et al.* reported that PEO [poly(ethylene oxide)] crosslinked with urethane possesses better properties compared to PEO.[16–18] So, we decided to consider its use as a polymer matrix of a hybrid electrolyte.

In this paper, we have first investigated the swelling of PEO-urethane by an organic carbonate solvent in relation to the nature of this solvent (PC or DMC) and the lithium salt concentration. These two carbonates commonly used in batteries were chosen because their relative permittivity and donor number are different.

Although numerous papers report results of studies relevant to the properties of hybrid crosslinked electrolytes such as conductivity, electrochemical stability *etc.*,[13–15,19–21] few papers give information about the swelling of a crosslinked matrix by an organic solvent and how this swelling is affected by the concentration of a lithium salt in the solvent.

Little has been reported in the literature on obtaining composite electrodes from a polymer and a material by a chemical *in situ* crosslinking. Modifications should be obtained as it is well known that the morphology of the electrodes strongly affects battery behaviour.[22] Ionic–electronic conductivity is one of the most basic needs for an electrode material. So, the second objective of this work was to prepare some PEO-urethane–petroleum coke composites with electrical conductivity. Finally, we investigated their electrochemical behaviour in an organic electrolyte in experimental conditions close to a hybrid electrolyte.

Experimental

Products

PEO with a molecular weight of 2000 was supplied by Merck. The crosslinking agent (Desmodur RE kindly supplied by Bayer) was a solution of 4,4′,4′-methylidynetris(phenyl isocyanate) in diethyl acetate.

The synthesis of the PEO-urethane network was done according to an experimental procedure already reported,[16–18] in a glovebox in order to eliminate side reactions due to water. The viscous mixture was cast between two glass plates separated by a flat spacer (1 mm) to control the thickness of the membrane. After one day at room temperature, the membrane was then vacuum dried at 80 °C.

Propylene carbonate (PC from Fluka), dimethyl carbonate (DMC from Merck) or their mixtures with ethylene carbonate (EC from Merck) were stored over molecular sieves, previously activated at 200 °C in order to lower their water content. $LiCF_3SO_3$ (from 3M) was dried at 100 °C under vacuum prior to use. $LiAsF_6$ (from Lith Co) was used as received. The composition of the mixtures is given hereafter in volumes of solvents.

Petroleum coke type PC 40 with an average particle size of 14 µm was kindly supplied by Lonza.

Apparatus

Conductivity measurements (DC and AC) were made using a PAR 273 apparatus from EG&G coupled with a Schlumberger analyser in a frequency range of 10^5 to 1 Hz or with a multimeter. The membrane was sandwiched between two blocking stainless steel electrodes in a home made cell[18] which allows us to work under argon.

A 'Mac Pile' system (from Bio-Logic Co) that can operate either in a galvanostatic or a potentiostatic mode was used to perform electrochemical experiments. Coin cells were constructed using a working electrode based on coke, a Celgard 2400 microporous film (as separator), a Viledon foil (as electrolyte reservoir) and a lithium foil (from Aldrich) which acts as counter electrode and reference electrode. Working electrodes were either a mixture of coke and Teflon (respectively 95 and 5% in weight) whose preparation has already been reported in,[23] or composite electrodes whose synthesis conditions will be described later. A volume of 300 µl of electrolyte was used during coin cell assembly which was done in an argon filled glovebox. $LiCF_3SO_3$ was used as it is less electroactive than $LiAsF_6$. All electrochemical data presented here concern coin cells tested at 45 °C. The potentials are expressed with respect to the Li^+/Li redox couple. Cycling tests were done between 2.5 and 0.010 V to avoid the oxidation of the electrolyte and the deposition of the metal lithium.

Determination of the transference number was done in the following concentration cell Li in PC–$LiAsF_6$ 1 mol l^{-1}//carbonate–$LiAsF_6$ C_1//PEO//carbonate–$LiAsF_6$ C_2 //Li in PC–$LiAsF_6$ 1 mol l^{-1}.

Briefly, the PEO-urethane membrane was sandwiched between two carbonate electrolytes with a difference in the lithium concentration (C_1 and C_2). C_1 and C_2 were varied between 0.1 and 0.9 mol l^{-1} so that the average concentration $(C_1+C_2)/2$ was always 0.5 mol l^{-1}. Two lithium threads (Li) immersed in a separate compartment containing PC–$LiAsF_6$ 1 mol l^{-1} were used to measure the cell voltage with a Tacussel millivoltmeter. The first and last measurements were done with the same electrolyte on both sides of the membrane to verify that we worked under equilibrium conditions with no deterioration of the membrane.

SEM micrographs were recorded with a Philips XL 30 scanning electron microscope.

Results

Behaviour of PEO-urethane in a carbonate electrolyte

Weight increase of PEO-urethane with a carbonate electrolyte. Using PEO network instead of linear PEO gives rise to the problem of salt and solvent incorporation in the material. To understand and control this process, we studied the swelling of PEO based networks dipped in organic carbonate electrolytes. Samples of the PEO-urethane membranes of 10 mm diameter were dipped for different durations in 10 cm^3 of solutions based on a lithium salt ($LiAsF_6$) dissolved in PC or DMC solvent. The penetration of the solution in the membranes of PEO-urethane was measured by weighing samples before and after immersion. The results are given in Fig. 1–3 and are expressed in weight increase defined as $[(m-m_0)/m_0]$ with m the weight of the swollen membrane and m_0 the weight of the membrane before swelling as reported elsewhere.[24] Each polymer chain was assumed to have 44 ethylene oxide units between crosslinks, which allows comparison of the network behaviour. Furthermore, the thermal history of the networks was assumed to be the same. The influence of the crystallinity, known to slow down the diffusion process of a solvent in a semi crystalline network, was then assumed to be the same in each network and to have a negligible effect. Considering the low amount of extractible products, one can assume that free chains do not influence the measurements.

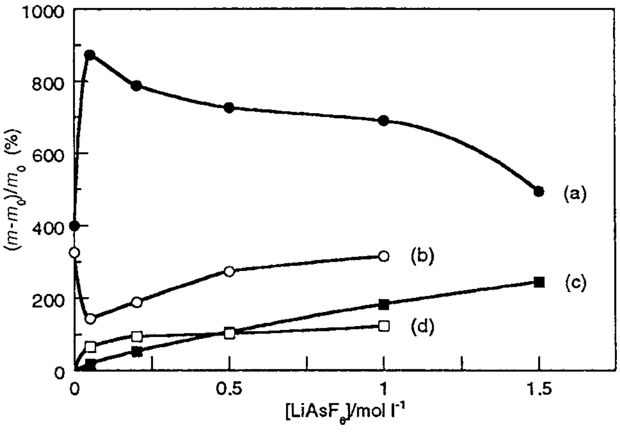

Fig. 1 Dependence of the weight increase of PEO-urethane samples on the concentration of $LiAsF_6$ after an immersion time of 2300 min: (a) without drying, in PC based solutions; (b) without drying, in DMC based solutions; (c) with drying, in PC based solutions; (d) with drying, in DMC based solutions

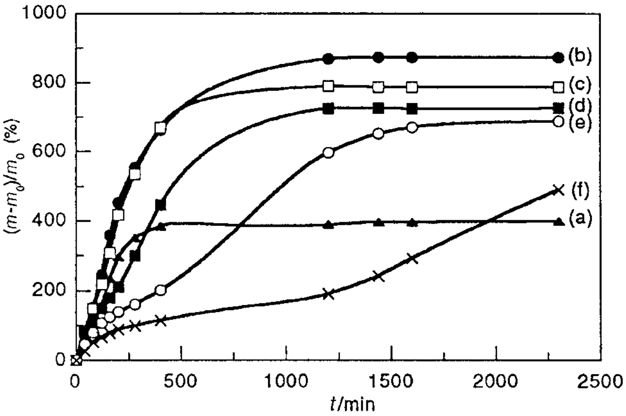

Fig. 2 Dependence of the weight increase of PEO-urethane samples on their immersion time in PC based solutions with the following concentrations of $LiAsF_6$: (a) 0, (b) 0.05, (c) 0.2, (d) 0.5, (e) 1, (f) 1.5 mol l^{-1}

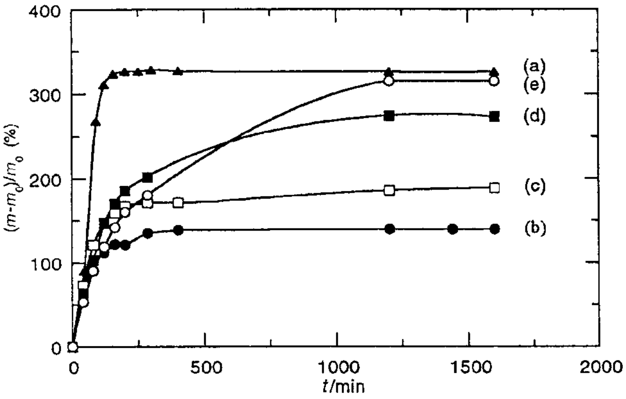

Fig. 3 Dependence of the weight increase of PEO-urethane samples on their immersion time in DMC based solutions with the following concentrations of $LiAsF_6$: (a) 0, (b) 0.05, (c) 0.2, (d) 0.5, (e) 1 mol l^{-1}

Fig. 1 shows the weight increase of PEO-urethane membranes as a function of the concentration of $LiAsF_6$ dissolved in DMC or PC solvents for a dipping time of 2300 min. This time is sufficient to reach thermodynamic equilibrium as will be discussed further. The weight increase of the PEO-urethane membranes due to the salt plus solvent increased with the $LiAsF_6$ concentration for DMC solutions (b) but reached a maximum for PC solutions (a), at 0.05 mol l^{-1}. The amount of incorporated electrolytes (PC or DMC) is much larger than would be expected using linear PEO, of adequate size and mechanical properties.[15] Drying the PEO-urethane membranes leads to the determination of the amount of $LiAsF_6$ incorporated in those membranes. PC based solutions (c) allowed a higher salt uptake than DMC based solutions (d) when the $LiAsF_6$ concentrations were high. However, it is worth noting that the salt uptake was higher with DMC based solutions when the $LiAsF_6$ concentration was low. Comparison of curves (a) and (c) shows that salt uptake in PEO based networks increases with $[LiAsF_6]$ in PC solutions, despite the decrease of the solvent plus salt uptake. This behaviour can be explained by a strong interaction between the salt and the chains of the network: the elasticity of the network decreases with salt uptake, reducing the equilibrium swelling. Curves (b) and (d) dealing with DMC solutions showed a different trend: both uptakes increased with $[LiAsF_6]$. The ratio between the two uptakes is constant: 2 moles of DMC per mole of salt. The diffusive species, assumed to be a molecule of salt solvated by two molecules of solvent [referred to hereafter as $LiAsF_6\cdot(DMC)_2$], might have a high interaction with the PEO network, preventing any measurable incorporation of free solvent molecule. In other words, this behaviour results from the Flory parameter of interaction between the chains swollen by $LiAsF_6\cdot(DMC)_2$ and the free solvent molecules being too large.

To further understand these phenomena, the weight uptake of PEO-urethane membranes in solutions based on PC and DMC was determined (respectively Fig. 2 and 3) with different $LiAsF_6$ concentrations as a function of the dipping time. Comparing first the weight increase of the PEO-urethane membranes immersed in solvents (PC or DMC) without lithium salt gives indications of the solvent–PEO-urethane interactions. The amount of solvent which is incorporated in these membranes is higher for PC than for DMC due to a higher affinity of the PEO based macromolecular chains with PC. The initial slope of the solvent uptake is indicative of the diffusion kinetics; comparing Fig. 2 and 3 indicates that the diffusion rate of DMC is slightly faster than that of PC. Obviously, the strong interaction between PEO units and PC molecules is detrimental to the rate of PC diffusion.

Fig. 2 shows the salt plus solvent uptake of some PEO-urethane membranes dipped in solutions based on PC with different $LiAsF_6$ concentrations. For each salt concentration, the equilibrium swelling was reached within less than 2300 min except for the highest concentration. A slowing of the diffusion process is observed with increased salt concentration: evidence of the strong interaction between the diffusing salt and the polymer host. The role of the PC solvent seems to be the reduction of the local viscosity of the network since the initial rates of diffusion are slightly higher for PC solutions than for DMC at low salt concentration. Kinetics and thermodynamics show that the weight increase behaviour of the PEO-urethane dipped in PC solutions is controlled by the interactions between the lithium salt and the PEO chains.

When the solvent was DMC (Fig. 3), the diffusion into the PEO-urethane membranes was much faster than with PC and the equilibrium swelling was reached within 1500 min, irrespective of the salt concentration. The diffusion slowed with increasing salt concentration [Fig. 3(b–e)]. At the start of the dipping experiments, both DMC and complexes are diffusing in the PEO-urethane membrane but the diffusion of DMC is rapidly stopped due to an increase of the concentration of $LiAsF_6\cdot(DMC)_2$ complex in the membrane. Kinetics experiments reveal a good interaction of the complex with the PEO chains.

We suggest that the weight increase of PEO-urethane membranes immersed in $LiAsF_6$ solutions depends on the nature of the carbonate solvent: the diffusion is clearly controlled by the PEO-urethane–lithium salt interactions with PC based solutions and by the PEO-urethane–$LiAsF_6\cdot(DMC)_2$ interactions with DMC based solutions.

Since the use of $LiAsF_6$ is becoming prohibited in lithium battery applications, we also conducted experiments with $LiCF_3SO_3$ as lithium salt. The same dependence of the weight uptake in relation to the carbonate and the salt concentration was obtained but the concentration range investigated was narrower because the solubility of $LiCF_3SO_3$ is low in DMC (0.3 mol l^{-1}).

Mixtures of solvents are usually used in lithium batteries to obtain an electrolyte with good conductivity, low reactivity towards the electrode materials and ability to operate over a large temperature range. So, we decided to extend this study to mixtures of carbonates derived from PC–EC–DMC (1 : 1 : 3) which we usually used in coin cells,[23] to produce hybrid electrolytes of interest in the field of batteries. EC is solid at room temperature and can only be used when mixed with another solvent. The influence of various solvent ratios was then tested, but the participation of each solvent in the mixture on the weight uptake is difficult to estimate.

Table 1 gives the percentage of weight increase measured for PEO-urethane samples after a 48 h immersion in mixtures of carbonates in the absence and in the presence of a lithium salt at 1 mol l^{-1}. The EC–DMC mixture (1 : 3 in volume), with or without the lithium salt, leads to the lowest percent weight increase. However, the $LiCF_3SO_3$ incorporated in the PEO-urethane network does not vary significantly with the mixture compositions but a slight variation is observed when $LiAsF_6$ is used. The mixture of EC–DMC (1 : 3 in volume) is then used for the electrochemical study in order to control the amount of incorporated salt and to keep the swelling low.

Conductive properties of hybrid electrolytes based on PEO-urethane and a carbonate solvent. The use of PEO-urethane–carbonate membranes as a hybrid electrolyte in lithium batteries assumes that they ensure the transport of charged species including lithium species. Here, we have used the concentration cell method to measure the transference number of the ions; it is a potentiometric technique in which the electrolyte undergoes no perturbation because no current is applied. $LiAsF_6$ was chosen because of its good solubility in DMC.

The concentration cell method has already been developed in the literature for polymer electrolytes.[25–27] Hypotheses are as follows: (i) the ionic motions are only due to the concentration gradient, (ii) the activity coefficients are approximately the same in the two electrolytes. The voltage due to the difference in concentration is expressed as eqn. (1)[27]

$$\Delta E = RT/F\ (t_{Li^+} - t_{AsF_6^-})\ \ln(C_1/C_2) \qquad (1)$$

In our experimental cell presented in the experimental section, junction potentials exist due to the separate compartments; deviations of the Nernstian law were also observed for the Li^+/Li redox system in relation to the salt concentration. Elimination of these perturbations was obtained by subtracting the cell voltages obtained with a Celgard membrane and with a PEO-urethane membrane. This consequently allows us to compare the behaviour of the PEO-urethane membrane with reference to membranes used in commercially available batteries. A plot of $(\Delta E_{\text{PEO-urethane}} - \Delta E_{\text{Celgard}})$ against log (C_1/C_2) is linear and the slope gives access to Δt_{Li} (*i.e.* t_{Li} with PEO-urethane membrane $- t_{Li}$ with the Celgard membrane). No cell voltage is measured when a Celgard membrane is sandwiched between two solutions of PC with different salt concentrations. This result suggests that the Celgard acts as an inert membrane.

Table 2 gives Δt_{Li} values for different solvents. PEO-urethane and Celgard are both swollen by the carbonate electrolyte so

Table 1 Weight increase (%) of the PEO-urethane samples after 48 h of immersion in the solution (composition of mixture is expressed as volume of solvent)

composition of the carbonate mixture		weight uptake (%) in solvent mixture	weight uptake (%) in $LiAsF_6$ 1 mol l^{-1}–solvent mixture		weight uptake (%) in $LiCF_3SO_3$ 1 mol l^{-1}–solvent mixture	
			before drying	after drying	before drying	after drying
EC–DMC	1:3	400	453	155	210	110
	1:1	413	547	159	—	—
	3:1	393	622	159	—	—
PC–DMC	1:3	352	409	143	213	102
EC–PC	1:1	369	646	177	358	117
PC–EC–DMC	1:1:3	388	—	—	273	166

Table 2 Dependence of Δt_{Li} on solvent (the composition of the mixture is expressed as volume of solvent)

Solvent	Δt_{Li}
PC	−0.2
DMC	0
PC–EC–DMC (1:1:3)	−0.10
EC–DMC (1:3)	−0.12
PC–DMC (1:3)	−0.12

that negative or positive values of Δt_{Li} can be attributed to a solvation of the species by the polymer. With PC, the Δt_{Li} value suggests that some interactions exist between the lithium species and the polymer. This would assume that the polymer interacts more strongly than PC with the lithium species so that lithium species move preferentially hopping from one oxyethylene unit to another through the breaking and the forming of cation–oxygen bonds. This result agrees well with the weight increase results and the results on hybrid electrolytes reported by other authors[28–30] who have observed no Li–PC interactions in the presence of a polymer. With DMC, Δt_{Li} is close to zero, suggesting a preferential solvation of the lithium species by the carbonate. This would imply that the lithium species move through the polymer matrix in a solvation shell of the carbonate molecules. This preferential solvation is consistent with a donor number for DMC higher than the donor number for PEO and PC and with the weight increase results and the literature relative to hybrid electrolytes.[28–30] With EC–DMC (1:3 in volume) mixture, PC–DMC (1:3 in volume) mixture or PC–EC–DMC (1:1:3 in volume), Δt_{Li} has an intermediate value.

Synthesis and characterisation of composite PEO-urethane–petroleum coke electrodes

Synthesis of composite electrodes. PEO and coke were first dried at 80 °C under vacuum for 48 h. The appropriate weight fractions of PEO and coke were added to CH_2Cl_2 in small excess. PEO dissolves in CH_2Cl_2 to produce homogeneous mixture. This mixture was allowed to stand in contact with air for a few days at room temperature to eliminate the solvent and it was finally dried under high vacuum for 24 h at 80 °C. The polycondensation reaction was done with the procedure reported in the experimental section. Only the ratio of the volume of reactants to the (volume of reactants + volume of CH_2Cl_2) was modified because of the presence of coke; it was fixed at 0.6 to avoid bubble formation and syneresis.

The PEO weight content was varied between 25 and 75%. The 25% value was chosen according to data available in the literature which suggest that with decreasing precursor ratio, the probability of encounter also decreases to the point (generally around 25%) where no more reaction (polycondensation or gelation) is possible.[31].

Fig. 4 shows SEM micrographs for composite electrodes without (a) or with PEO-urethane (b and c). Coke particles are clearly observed without PEO (a) or when the PEO-urethane content is below 50% (c). The two faces of a same composite electrode differ slightly (b1 and b2, c1 and c2) when its bulk structure is homogeneous (b3 and c3).

Electrical conductivity of composite electrodes. Composite electrodes must exhibit some electrical conductivity to be used in batteries with good efficiency. This is allowed by adding conductive coke particles to the polymer at weight loadings above a threshold called 'the electrical percolation weight loading' which corresponds to the formation of a continuous path of conductive particles where the electrons can flow.[32–40]

The change in resistivity with coke loading (expressed as weight or volume fraction) is illustrated in Fig. 5. The electrical percolation weight loading is close to 46%. The transition from non-conductive to conductive composite electrodes with a constant value of resistivity extends over the 46–75% range.

The theory regarding spherical carbon black systems predicts that the percolation occurs at around 40% by weight of carbon (34% volume of carbon)[39] but it is well established that many parameters influence the percolation threshold of composite materials such as filler–matrix interactions, filler shape and spatial distribution of the filler. The amorphous and polar characteristics of PEO-urethane are detrimental to the percolation as they encourage a uniform distribution of the coke in the polymer. Moreover, crosslinking is known in the literature to increase the resistivity and the percolation threshold of composites.[32] The size of the coke particles in this study is also detrimental to the percolation as it is at least two orders of magnitude above that of carbons used in other studies. All these parameters contribute to increase the electrical percolation weight loading up to 46% by weight of coke.

Electrochemical behaviour of the composite electrodes. Composite electrodes were electrochemically tested finally in the presence of a mixture of carbonates. Our preliminary tests have shown that they were electrochemically inactive when PC was used in the mixture. This suggests that the swelling with mixtures based on PC causes the separation of the conductive particles into the composite electrodes reducing their electrical conductivity, as already reported in.[41] This is due to an expansion of the polymer that reduces the coke concentration on a volume basis. Our electrochemical results agree well with experimental data given in ref. 1 as large weight increases are obtained with mixtures based on PC.

So, in this study, we selected: (i) an EC–DMC mixture as it gives a smaller weight increase with the PEO-urethane and it is commonly used in lithium batteries and (ii) the composite electrode with the highest coke loading to maintain electrical conductivity. Electrochemical studies for coke without polymer (referred to hereafter as latex) are also reported for reference.

Fig. 6(a) and (b) show voltammograms obtained for both electrodes. Reduction occurs in two main steps, already attributed in the literature.[11–23] Comparing these figures shows that PEO-urethane has no influence on the potentials of these

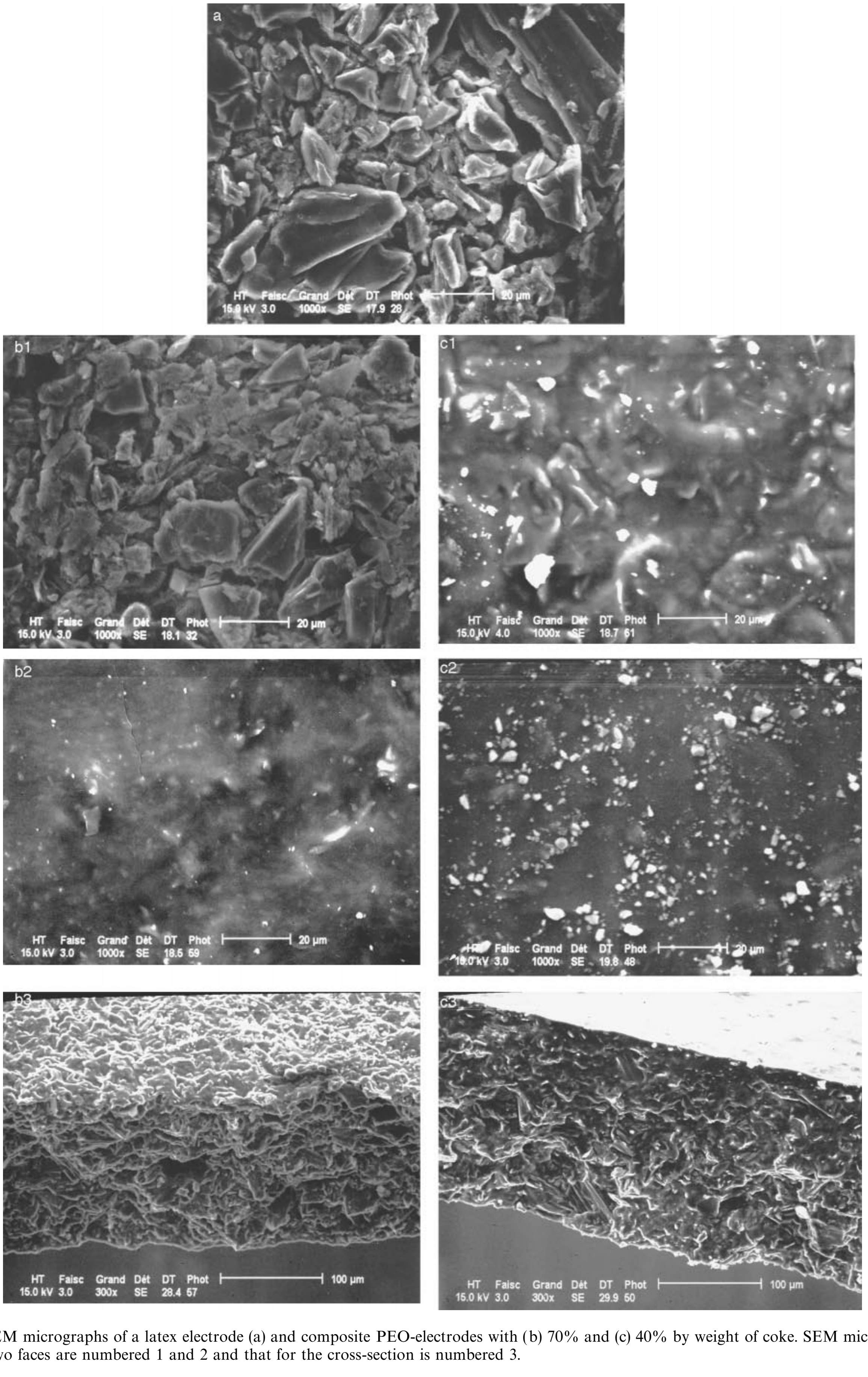

Fig. 4 SEM micrographs of a latex electrode (a) and composite PEO-electrodes with (b) 70% and (c) 40% by weight of coke. SEM micrographs for the two faces are numbered 1 and 2 and that for the cross-section is numbered 3.

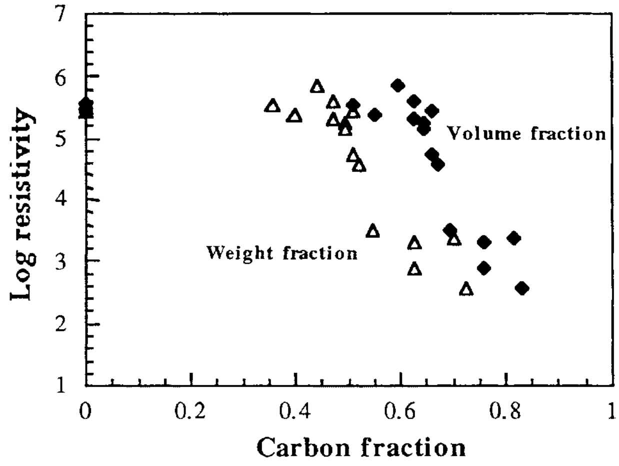

Fig. 5 Dependence of the composite electrodes onto the coke fraction expressed in weight or volume

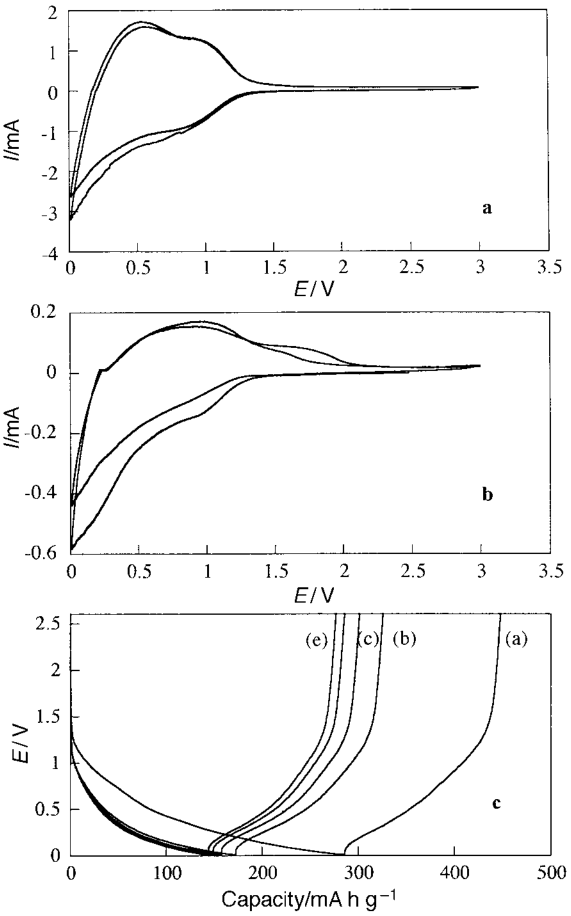

Fig. 6 (a) and (b) Voltammograms obtained with a latex electrode (a) and a composite electrode (70% by weight of coke) (b), scan rate of 3.6 mV mm^{-1}. (c) Cycling curves obtained on a composite electrode (70% by weight of coke), current density of 380 μA cm^{-2}; the letter corresponds to the cycle number. EC–DMC (1 : 3 v/v), $LiCF_3SO_3$; 1 mol l^{-1}

electrochemical processes. Reoxidation also occurs in two main steps but their potentials are shifted towards higher values with the composite electrode. The second reduction scan for both electrodes differs from the first scan; this has already been attributed to the formation of a passivating layer on the lithiated coke along with the first lithium insertion. It is obvious that PEO-urethane does not suppress the passivation phenomenon of the lithiated coke.

Fig. 6(c) gives the first five reduction–reoxidation cycles for a composite electrode. The capacity varies abruptly between the first and second cycle. It fades more slowly during subsequent cycles.

The faradic capacity for the first reduction is 290 m Ah g^{-1} for the composite electrode and 350 m Ah g^{-1} for the latex electrode. Several causes can explain this difference: (i) some coke particles may be isolated from the conductive network and are not involved in the electrochemical processes, (ii) the end of the lithium insertion into the coke occurs at potentials lower than the voltage limit because of the presence of PEO-urethane.

Cycling results permit the calculation of the capacity loss. A large capacity loss is found during the first cycle and it is lower during the subsequent cycles (respectively 32, 9, 6 and 5%). This confirms that part of the capacity engaged during the first reduction corresponds to some irreversible processes (reduction of the electrolyte or its impurities directly or indirectly with the lithiated coke); the passivation layer on the composite electrode originates from the insoluble products of these processes. These irreversible processes are minor as cycling proceeds because of the passivating layer.

Table 3 gives the faradic efficiencies for the first and the fifth cycle as a function of the current density. Contrary to all expectations, the faradic yields decrease when the current density is lowered, *i.e.* when the contact time between the lithiated composite electrode and the electrolyte increases. This suggests that the passivating layer limits but does not stop the reactions between the lithiated composite electrode and the electrolyte.

Lithium stability in the latex electrode or in the composite electrode was also studied using the following experimental procedure: five reduction–reoxidation cycles were performed to generate the passivating layer followed by a final reduction. The reduced electrodes were thererafter stored at open current voltage before electrochemical reoxidation was done. No improvement of the lithium stability was obtained with the composite electrode (Table 4). So, one can assume that the passivating layer is not effective in the lithium protection due to its heterogeneous nature as PEO-urethane and the products resulting from the reactions between lithium and PEO-urethane or the organic electrolyte help to make up its composition. The less protective properties of a heterogeneous layer have already been reported in the literature for mixtures of organic solvents.[42,43] Finally, our results suggest no superiority of hybrid electrolytes based on PEO-urethane over liquid electrolytes when coke is used as anode.

Table 3 Faradic efficiency values (%) of the first and the fifth reduction–reoxidation cycle as a function of the current density. EC–DMC (1 : 3 v/v); $LiCF_3SO_3$, 1 mol l^{-1}. Composite PEO-urethane–petroleum coke (30 : 70) electrode

current density/ mA cm^{-2}	faradic yield (%) of the first cycle	faradic yield (%) of the fifth cycle
300	68	95
200	70	95
160	68	94
100	67	89
60	55	88

Table 4 Lithium loss obtained during storage in EC–DMC (1 : 3 v/v), $LiCF_3SO_3$, 1 mol l^{-1} of a composite and a latex reduced electrode

Storage time/hours	% of lithium loss with a composite electrode	% of lithium loss with a latex electrode
250	18	9
500	40	20

Conclusion

Our results show that the nature of the carbonate governs the swelling of the PEO-urethane and the solvation of the lithium species. Results indicate that the diffusion of a liquid electrolyte in the polymer is clearly controlled by the PEO-urethane–lithium salt interactions with PC based solutions and by the PEO-urethane– $LiAsF_6.(DMC)_2$ interactions with DMC based solutions.

An electrically conductive electrode based on PEO-urethane and petroleum coke calls for a higher carbon loading than that reported in the literature for carbon–polymer composites. This is due to the particle size of the coke and to the reticulated and amorphous structure of the PEO-urethane which enhances a uniform distribution of the carbon particles. PEO-urethane has a minor influence on the electrochemical behaviour of coke in a carbonate mixture but it decreases the stability of the lithiated coke. An improvement of this stability requires the use of a dry PEO-urethane electrolyte. Studies regarding these composite electrodes in a solid PEO-urethane electrolyte are now in progress in our laboratory.

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