Journal of Power Sources 326 (2016) 285–295

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Role of PF_6^- in the radiolytical and electrochemical degradation of propylene carbonate solutions

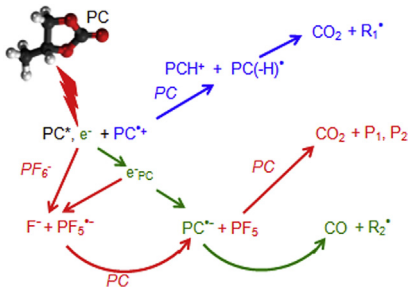
Daniel Ortiz [a], Isabel Jimenez Gordon [b], Solène Legand [c], Vincent Dauvois [c], Jean-Pierre Baltaze [d], Jean-Louis Marignier [e], Jean-Frédéric Martin [b], Jacqueline Belloni [e], Mehran Mostafavi [e], Sophie Le Caër [a, *]

[a] LIONS, NIMBE, UMR 3685, CEA, CNRS, Université Paris-Saclay, CEA Saclay Bât. 546, F-91191 Gif-sur-Yvette Cedex, France
[b] CEA/LITEN/DEHT/SCGE, F-38000 Grenoble, France
[c] CEA/DEN/DANS/DPC/SECR/LRMO, F-91191 Gif-sur-Yvette Cedex, France
[d] Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Bât. 410, F-91405 Orsay Cedex, France
[e] Laboratoire de Chimie-Physique/ELYSE, UMR 8000 CNRS/UPS, Université Paris Sud, Bât. 349, F-91405 Orsay Cedex, France

HIGHLIGHTS

- The presence of $LiPF_6$ in PC significantly affects the decomposition pathways.
- CO_2 production is doubled in irradiated PC/$LiPF_6$ 1 M as compared to irradiated PC.
- This effect is specific of $LiPF_6$ and is not observed in other salts such as $LiClO_4$.
- A high reaction rate constant between the electron and PF_6^- in PC is measured.
- Radiolysis accelerates aging and enables the description of reaction mechanisms.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 April 2016
Received in revised form
20 June 2016
Accepted 28 June 2016
Available online 9 July 2016

Keywords:
Propylene carbonate
Pulse radiolysis
Electrolysis
Li-ion battery
Anion effect
Degradation reaction mechanisms

ABSTRACT

The behavior under irradiation of neat propylene carbonate (PC), a co-solvent usually used in Li-ion batteries (LIB), and also of Li salt solutions is investigated. The decomposition of neat PC is studied using radiolysis in the pulse and steady state regime and is assigned to the ultrafast formation, in the reducing channel, of the radical anion $PC^{\bullet -}$ by electron attachment, followed by the ring cleavage, leading to CO. In the oxidative channel, the PC(−H)• radical is formed, generating CO_2. The CO_2 and CO yields are both close to the ionization yield of PC. The CO_2 and CO productions in $LiClO_4$, $LiBF_4$ and $LiN(CF_3)_2(SO_2)_2$ solutions are similar as in neat PC. In contrast, in $LiPF_6$/PC a strong impact on PC degradation is measured with a doubling of the CO_2 yield due to the high reactivity of the electron towards PF_6^- observed in the picosecond range. A small number of oxide phosphine molecules are detected among the various products of the irradiated solutions, suggesting that most of them, observed in carbonate mixtures used in LIBs, arise from linear rather than from cyclical molecules. The similarity between the degradation by radiolysis or electrolysis highlights the interest of radiolysis as an accelerated aging method.

* Corresponding author.
E-mail address: sophie.le-caer@cea.fr (S. Le Caër).

http://dx.doi.org/10.1016/j.jpowsour.2016.06.122
0378-7753/

1. Introduction

In a world where the reserves of fossil fuels are limited, the conversion and storage of energy is necessary. Electrochemical batteries enable this storage [1]. Among them, lithium-ion batteries (LIB) are increasingly used as they have very high energy densities [2–4]. Nevertheless, they exhibit safety issues. Moreover, for a full exploitation of them in electric and hybrid vehicles, a higher energy density and a longer lifetime are required. It is therefore crucial to have an in depth understanding of the aging phenomena occurring in LIBs. Until now, many of the works trying to unravel degradation mechanisms have focused on the electrolyte degradation with the LIB functioning for long periods followed by final products analysis using different techniques such as mass spectrometry (MS) [5–7], nuclear magnetic resonance (NMR) [8,9], or calculations/simulations [10–12]. Usually, these studies are lengthy, costly and most often essentially qualitative [13].

We have recently demonstrated that radiolysis is an adequate tool to accelerate and mimic the aging process in electrolytes [14,15]. Instead of studying the electron transfer between the electrodes and the electrolyte that involves predominantly the Li^+ ions and also other components in an aging process, electrons and parent cations of the solvent produced in the radiolytical processes are directly and efficiently created in the bulk. In the pulse radiolysis regime, the primary transient species are observed using the time-resolved optical absorption technique and the ionization yield is quantitatively measured. Then, the analytical detection threshold of the final products is reached in the steady state radiolysis regime at high dose rate at much shorter time than using electrolysis. Such decomposition processes, including the role of the $LiPF_6$-containing electrolyte, have been first studied in a linear carbonate, diethyl carbonate ($C_2H_5OCOOC_2H_5$, labeled as DEC) [14,15]. The purpose of the present work is to decipher now the degradation processes in the cyclical propylene carbonate ($[OCOOCH_2CH]_c(CH_3)$ labeled as PC), with a focus on the role of the lithium salts.

Indeed, cyclical carbonates, such as propylene carbonate or ethylene carbonate (EC), are essential in LIBs because of their physical properties such as their high melting point (242/248 °C) or their high dielectric constant (ε_s = 66/90) [16]. Moreover, it has been reported that they play an important role in the solid electrolyte interface (SEI) formation or in the decomposition processes [17]. These processes are based on the formation of radical anions [18,19], contrary to linear carbonates where are readily formed radical cations [14,15]. Lastly, recent calculations pointed out that the interaction between the salt and PC plays a critical role in the decomposition pathways and that the nature of the anion can change drastically the decomposition thermodynamics, then the rates and the nature of the products [12]. This is in line with previous experimental and theoretical studies demonstrating that the oxidation products of PC are independent of the nature of the salt, but that their decomposition rate will change depending on the salt [20,21]. However, the influence of the salt on the oxidative electrolyte degradation is still under debate. On one hand, it was shown using graphite powder as a working electrode that the gas generation was enhanced in the PC/$LiClO_4$ system compared to neat PC, whereas a lower gas volume was measured in the presence of $LiBF_4$ and even a still lower value for $LiPF_6$ than for $LiClO_4$ [22]. On the other hand, the oxidation of PC was studied on a $LiCoO_2$ thin electrode [20]. In this case, the oxidation of PC with $LiPF_6$ was shown to be the most severe, whereas it was lower with $LiBF_4$.

The aim of this work is to benefit of the advantages of the radiolysis approach [15] to analyze, after hours (gamma source) or half an hour (electron beam) of irradiation in the steady state regime, the degradation products and to compare them with those of the electrochemical degradation in LiBs, because it was demonstrated that very similar products are found in both radiolytical and electrochemical processes (same molecules, though more rapidly produced by radiolysis). In addition, the picosecond pulse radiolysis regime and transient analysis provide new and useful information to decipher the early stages of the electron transfer mechanisms that are out of reach by either electrochemistry or steady state radiolysis. This short and long-time scale strategy allows understanding the degradation mechanisms in neat PC and the role of different lithium salts on very large timescales.

For this purpose, picosecond pulse radiolysis coupled with time-resolved spectroscopy was performed to unravel the primary phenomena at short time scales. At long time scales, the liquid and gas phases were analyzed by using gas chromatography, mass spectrometry and nuclear magnetic resonance techniques. Lastly, in the case of PC/$LiPF_6$, the results obtained by radiolysis were also compared with those obtained by electrochemical degradation. All these experiments enable us to propose reaction mechanisms for the degradation processes in PC as well as to investigate the effect of the nature of the anion present in solution.

2. Experimental procedures

2.1. Chemicals and sample preparation

Battery grade solutions of 1 mol/L $LiPF_6$ in PC (density 1.31 g/ml at 25 °C), neat PC (anhydrous, 99.7%), $LiClO_4$ (anhydrous, 99.99%), $LiBF_4$ (anhydrous, 99.99%) of the highest available purity were purchased from Sigma Aldrich and used as received. $LiN(CF_3)_2(SO_2)_2$ (extra dry, 99.99%) was obtained from Solvay. Water concentration, measured by a coulometric-Karl Fischer titration, was systematically measured and was never higher than 20 ppm. Solutions were prepared in an argon-filled glove compartment without further purification. Preparation details were described elsewhere [14,15].

2.2. Picosecond pulse radiolysis at ELYSE

The ultrafast kinetics in the solutions was accessed by picosecond pulse radiolysis using the laser-driven electron accelerator ELYSE. The pump-probe detection setup is extensively detailed elsewhere [23]. The transient absorbance of the samples is probed in a flow cell with 5 mm nominal optical path, collinear to the electron pulse propagation. The electron pulses are delivered with a pulse duration of about 10 ps and an electron energy of 7.6 MeV at a repetition rate of 10 Hz. The system is operated in two different configurations for continuum light generation. Single crystals of CaF_2 for the visible and of yttrium aluminum garnet (YAG) for the NIR are used. More technical specifications about both configurations are largely described elsewhere [24]. The dose per pulse during the experiments is deduced from the absorbance of the hydrated electron e^-_{aq} in water [25]. During these experiments the dose in water D_w was typically around 50 Gy (1 Gy = 1 J kg^{-1}) per pulse. The doses received, as expressed in Gy are the same in water and in PC, or as expressed in J L^{-1} are 20% higher in PC than in water.

2.3. Irradiation experiments using γ–rays and 10 MeV electrons

Similarly to our previous works [14,15], the irradiation experiments to measure the gas-phase stable decomposition products were currently performed by a MDS Nordion Gammacell 3000 ^{137}Cs source. The dose rate, determined using the Fricke dosimeter, is 5 Gy/min [26]. Therefore, the 20 kGy maximum dose used in the present work is reached within 67 h (i.e. 2–3 days). As to the liquid decomposition products, they were obtained by using the repetitive 10 ns electron pulses of a Titan Beta, Inc. accelerator, which was