Dimethyl carbonate (DMC) electrolytes – the effect of solvent purity on Li–ion intercalation into graphite anodes

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Abstract

Graphite electrodes cycled in single solvent electrolytes based on dimethyl carbonate (DMC) exhibit surprising and unfamiliar behavior. The electrochemical performance of graphite anodes cycled vs. Li metal in DMC electrolytes, containing 1 M LiPF₆ is strongly dependent on the solvent purity. The behavior of the graphite anodes in electrolytes containing “pure” DMC is dependent mainly on the identity of the contamination present in the native solvent. It was found that methanol is causing deterioration in the electrochemical performance of the cycled graphite electrode, while carbon dioxide and mainly carbonochloridic acid methyl ester are enhancing the performance. It was established that it is essential to investigate and understand the processes and materials used during the production of battery grade solvents, in order to clarify the roll of traces of chemical compounds responsible for the variation and modification in the electrochemical behavior of the cycled electrodes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Organic carbonates are considered to be the prime solvents used in nonaqueous energy conversion devices [1]. Many organic carbonate mixtures are used in order to enhance the electrolyte characteristics. Scheme 1 presents different organic alkyl carbonate used in research and production of energy devices. It is well known that ethylene carbonate (EC) is an important component in Li–ion battery electrolyte utilizing graphite electrode as the anode of choice [1–4]. The positive influence of EC on the graphite anode performance was ascribed to the presence of dilithium ethylene glycol dicarbonate, (LiOCO₂CH₂)₂, on the graphite anode surface as a reduction product of EC [5]. However, at least another solvent, low viscous, open chain alkyl carbonate is typically employed as an additional component in the solvent mixture [1–4].

In an earlier communication [6] we proposed a new model, the “Sticky Fingers” model, describing the interactions between the electrolyte reduction product structures and the protective films (called also SEI [7]) characteristics, formed on the graphite anodes in Li–ion electrolytes. In the proposed model, experimental observations related to the relations between the identity of the solvent/additives/electrolyte salt, used in Li–ion solutions and the electrochemical performance of the graphite anodes were considered. The “Sticky Fingers” model offers a rational explanation for the intermolecular interaction within the passive film itself and the specific interactions between the electrolyte reduction products and the graphite substrate. One of the cases studied was performed with the methyl alkyl carbonates [8–10]. We have observed that graphite anodes cycled in alkyl methyl carbonate solutions exhibit a superior performance, whereas no intercalation was observed in graphite cycled in alkyl ethyl carbonate electrolytes. Li alkyl carbonates were detected by FTIR [5,8,9] as the main reduction products of these solvents prior to the Li–ion intercalation process. We attributed the superior behavior of the graphite anodes cycled in alkyl methyl carbonate solutions to the fact that one of the possible
reduction products may be Li-methyl carbonate, formed on the graphite anode surface, without any loose ends, whereas in the case of larger Li-alkyl carbonates homologues (alkyl = ethyl, propyl, butyl) there is a loose alkyl tail which inhibit the formation of requisite compact film [6].

However, the results obtained from graphite electrodes cycled in dimethyl carbonate (DMC) solution were exceptional; the studies and the experimental observations obtained from graphite electrodes cycled in DMC electrolytes were reported to be poor [8,9]. The studies in [8,9] were conducted independently at two research centers; Bar-Ilan University (Israel) and Covalent Associates (MA, USA), while the source (manufacturer) of the DMC solvents was different. These studies showed, without any doubt, that graphite anodes are poorly cycled in single solvent electrolytes based on DMC as the solvent of choice. Surface studies showed that the major difference in the surface species formed on the graphite anode cycled in EMC and DMC is the cause of the difference in the electrochemical performance [8,9]. We have observed the formation of Li-alkyl carbonates and Li carbonate as the major film species produced on the graphite anode cycled in EMC electrolytes as a result of EMC reduction processes, while Li alkyl carbonate was observed to be the major reduction product of DMC.

Until now, we could not supply an explanation to the poor behavior of graphite cycled in single solvent electrolytes based on DMC and to the distinct difference in the surface science developed on the graphite anodes in DMC and EMC (6). The difference in the surface science developed on the graphite anodes and the fact that DMC was an exceptional alkyl methyl carbonate electrolyte, have driven us to thoroughly investigate the nature of the graphite anodes electrochemical performance observed in DMC electrolytes. For this purpose we obtained DMC from five different well-known battery solvents manufacturers.

2. Experimental

Carbon electrodes were prepared from synthetic graphite (SFG44, Timcal America) with theoretical capacities of 1.9–2.1 mA h. The graphite electrodes were tested as previously described [8–10]. DMC solvents (battery grade) were obtained from five different manufacturers and are named in alphabetical order (A–E). All solutions contained 1 M of LiPF₆ (Hashimoto) salt. Gas chromatograph (GC) tests were carried out with the use of HP GC system equipped with TC detectors. A cross-linked PEG (polyethylene glycol) capillary was used as a column. Gas chromatograph–mass spectroscoopy (GC–MS) of DMC was carried out with the use of Finnigan–Mat TSQ-70B system equipped with DB5-MS (30 m/0.25) column.

3. Results and discussion

3.1. Electrochemical performance of graphite electrodes in DMC single solvent electrolytes

Fig. 1 shows the charge/discharge profiles of graphite electrodes cycled vs. Li metal counter electrodes in DMC [A–E] solutions containing 1 M LiPF₆. Fig. 2 presents the slow scan cyclic voltammetry (20 μV/s) obtained from graphite electrodes during the first intercalation stage in DMC [A, D, E] electrolytes. Li metal electrodes were served as counter and reference electrodes.

The results are surprising; a clear correlation between the DMC source (manufacturer) and the electrochemical performance is shown. It appears to be that graphite electrodes cycled in two different electrolytes, containing DMC A and E, exhibit poor performance, while graphite electrodes cycled in electrolytes B–D showed superior results, complying with our earlier model prediction [6].
A deeper insight into the profiles obtained from DMC A and E shows that both of them, although being considered “poor”, exhibit different behaviors. Both the slow scan cyclic voltammetries, (Fig. 2) and the charge–discharge profiles (Fig. 1) are different. The irreversible potential plateau (measured at approximately 1 V) related to electrolyte components reduction and to the build-up of the passive films is much longer (almost twice the capacity) once the tested electrolyte is based on DMC A. The reversible capacities obtained from graphite electrodes cycled in DMC A electrolyte are higher than the reversible capacities obtained from graphite electrodes cycled in DMC E electrolyte. A careful look into the slow scan rate cyclic voltammetry (presented in Fig. 2) reveals the same observation. While graphite electrodes scanned in DMC B–D electrolytes (DMC D is a representative example) show all the reversible Li–ion intercalation peaks, the scans obtained from electrolytes A and E are somewhat “diffuse” and no clear peaks are visible. Again, the cyclic voltammetry obtained from graphite electrode cycled in DMC A is showing 3–4 “diffused” intercalation peaks, while the de-intercalation process is characterized with 2–3 super-positioned peaks, in agreement with the charge discharge profiles presented in Fig. 1. The difference in the observed irreversible capacities obtained during the first intercalation process may indicate that the mechanism of the graphite deterioration is different each time.

Scaling up (from bottom to top) the graphite electrode electrochemical performance in DMC single solvent electrolyte points out the following order: E → A → [B, C, and D]. The fact that a clear correlation between the electrochemical performance and the identity of the solvent manufacturer exists, forced us to investigate the solvent composition.

### 3.2. DMC purity-gas chromatograph measurements

Fig. 3(a) presents the chromatograms obtained from all DMC (A–E) solvents with the use of gas chromatograph (GC). The main solvent peak which appears at a retention time (RT) of 3.25 is not shown in Fig. 3. We have focused our GC studies in the RT regions prior and subsequent to the appearance of the main DMC solvent peak. While no peaks were observed in the chromatograms following the appearance of the main solvent
peak we have found some crucial differences in the chromatograms at early RT, prior to the appearance of the main solvent peak. The peak positioned at 0.9RT is related to the presence of air in the injection needle (approximately 100–120 ppm), which serves as a baseline. All of the chromatograms show a similar peak positioned at 1.25RT. The chromatogram obtained from DMC A and E is different from the chromatogram obtained from DMC B–D. The chromatogram obtained from DMC A shows only a minor peak at RT 1.25 (equivalent to 30–40 ppm) and insignificant peak at 1.75RT (less than 5 ppm) while the chromatogram obtained from DMC E shows a distinct peak at 1.75RT (∼450–500 ppm) and a more pronounced peak at 1.25RT (∼1500 ppm, while the measured concentration of this species in DMC B–D was 800–1000 ppm). In DMC group of B–D we also observed some differences; it is notable that in the chromatogram obtained from DMC B a small peak in 1.05RT is shown while in the other chromatograms this peak does not appear.

Our observation are with an excellent agreement with the electrochemical performance of graphite electrodes cycled in DMC single solvent electrolytes: DMC E has an additional chemical compound (1.75RT) which is causing the deterioration in the electrochemical performance of the graphite anode, while DMC A is lacking a species identified at 1.25RT which may influence the electrochemical performance of graphite electrodes cycled in this solution electrolyte.

The next step in our study was to identify the chemicals that are “added” (DMC E, 1.75RT) or “missing” (DMC A, 1.25RT), and also to identify the components responsible for the appearance of additional peaks present in the chromatograms of other solvents (1.05RT in DMC B). Fig. 3(b) shows the chromatograms obtained from air, CO, CO₂, methanol and water. The chromatogram obtained from DMC D is also shown in the upper chromatogram, for comparison. It appears that the additional peak at 1.75RT in the chromatogram obtained from DMC E is related to methanol. The small peak appears at 1.05RT in the chromatogram obtained from DMC B is actually CO₂. Based on the comparative results we can state that the electrochemical performance obtained from DMC electrolytes are directly affected by the purity of the so-called “battery grade” solvent. DMC form an azoetrope with methanol [11] and therefore, it is crucial to purify the DMC, since the presence of methanol, at these concentrations, may cause deterioration in the graphite electrochemical performance. Spiking electrolyte, based on DMC D, with 500 ppm of methanol causes the deterioration in the behavior of the graphite electrode polarized cathodically. The cyclic voltammetry profile obtained from this electrode is resembled to the profile obtained from graphite cycled in electrolyte based on DMC E, as shown in Fig. 2.

Another issue that we should pay attention to, is the solvent shelf life. The fact that DMC B contains low concentration of CO₂ points out that a dissociation of the alkyl carbonate may take place generating dissolved CO₂, which is a “positive” species forming highly protective film (Li₂CO₃), in accordance with spectroscopic studies [12,13].

We could not identify the chemical compound responsible for the appearance of the pronounced peak at 1.25RT only with the use of GC. However, it is obvious that the chemical compound represented by the 1.25RT peak is responsible for the enhancement of the electrochemical performance of graphite anodes in DMC electrolytes. This understanding is drawn from the only difference between chromatogram A and B–D; since the only difference in the chromatograms is the fact that the amplitude of the 1.25RT peak in chromatogram A is reduced significantly in comparison with the peak intensity produced from DMC B–D.

3.3. GC–MS analysis of DMC

In order to identify the chemical compound responsible for the 1.25RT peak appeared in DMC B–D...
chromatogram we analyze the chemical composition of DMC B–D with the use of GC–MS. Although the identity of this species was unknown until now, we succeeded in evaluating the chemical composition of DMC B–D. The identity of the 1.25RT peak was found to be related to the presence of a small amount of carbonochloridic acid methyl ester (ClCOOCH₃). The GC–MS data reveal the presence of a compound with a molecular weight of 94 with main fragments of 66, 62.9 and 59 g. The molecular structure of this compound was identified as carbonochloridic acid methyl ester (CAS 79-22-1). We assume that the reduction products of this compound precipitate on the graphite anode to form highly steady passive layer, allowing high reversible Li–ion intercalation. At this stage of the research we can only speculate on the nature of these compounds. Since carbonochloridic acid methyl ester is present in the solvent in very low concentrations, and since it is not commercially available, we could not further analyze the nature of the film produced on Li metal and carbon electrode in the presence of this compound. However, it should be emphasize that possible reduction products may include a mixture of Li₂CO₃, lithium methyl carbonate and LiCl. A possible reduction pathway of ClCOOCH₃ is shown in the following reactions:

\[
\text{ClCOOCH}_3 + e^- + \text{Li}^+ \rightarrow [\text{COOCH}_3]^+ + \text{LiCl}
\]

\[
[\text{COOCH}_3]^+ + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OLi} + \text{CO}
\]

CH₃OLi can further react with the solvent (DMC) to produce Li-methyl carbonate [9], while lithium carbonate can be produced via a direct reduction of Li-methyl carbonate, or via a secondary reaction with traces of water [8]. The presence of the carbonochloridic acid methyl ester also indicates the synthesis route of the DMC, involving the reaction between methanol and phosgene. The carbonochloridic acid methyl ester is a by-product of incomplete reaction between methanol and phosgene.

The data presented in this short communication reveal that Li–ion battery researchers and manufacturers must pay attention to a crucial (and a well known) factor which is the purity of the solvents used in the battery electrolyte. Moreover, some of these contaminants are causing deterioration (methanol) in the electrochemical performance of the graphite electrode, while others (carbon dioxide and mainly carbonochloridic acid methyl ester) are found to be highly beneficial.

4. Conclusions

We have presented some significant data on graphite electrodes cycled in a single solvent solution based on DMC. The electrochemical performance of graphite anodes cycled vs. Li metal in these electrolytes is strongly dependent on the solvent purity. Moreover, it is essential to investigate and understand the processes and materials used during the production of battery grade solvents, in order to point out on any chemical compounds that may be responsible for superior or poor behavior of the cycled electrodes and to thoroughly investigate and analyze the correlation between the composition of the currently produced solvents and the electrochemical performance obtained. The role of carbonochloric acid methyl ester as a passivating agent should be thoroughly explored and considered with the use of sophisticated surface techniques.

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References