

The effect of the Mn-ion oxidation state on propylene carbonate decomposition

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Abstract

Cyclic voltammetry revealed that the oxidation voltage of propylene carbonate (PC) containing 1 M LiClO₄ on MnO, Mn₂O₃ and MnO₂ is approximately 4.7 V. This suggests that the oxidation of PC is independent of the Mn-ion oxidation state. Gas chromatography results support the voltammetry results. CO₂ is the major gas evolved from the decomposition of PC on MnO, Mn₂O₃ and MnO₂. Reducing the oxidation state of the Mn-ion does not eliminate CO₂ gas formation in the Li/MnO₂ system. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Nonaqueous primary batteries with Li anodes and MnO₂ cathodes have been widely used in commercial applications since the early 1980s as a result of their high energy density, good rate capability, low-temperature performance, long-shelf life and competitive cost [1–5]. In general, Li/MnO₂ primary batteries are housed within a metal container. Recently, the US Army has become interested in the concept of a pouch cell for the Li/MnO₂ primary batteries. The pouch cell consists of the internal components sealed within a multilaminate of polyester, polyethylene, aluminum and surlyn [6–10]. Pouch cells offer the advantages of: (i) weight savings and (ii) improved safety compared to metal containers [10]. With the pouch cell comes many problems that were insignificant for Li/MnO₂ batteries housed within metal containers. One of these is the swelling of the pouch cells during storage prior to use.

Preliminary investigations suggest that the swelling of the pouch cells during storage is associated with gas generated by decomposition of the electrolyte solvent [7–9,11,12]. The most commonly used solvent is propylene

carbonate (PC). In this case, the gas most responsible for the swelling of the pouch cells during storage is CO₂ [8,11,12]. It has been suggested that one variable which effects solvent decomposition during storage is the Mn-ion oxidation state [8,11,13]. One method that has been proposed to decrease the extent of solvent decomposition and hence, gas formation is reducing the oxidation state of the Mn-ion [8]. However, no studies have been undertaken to confirm if indeed the oxidation state of the Mn-ion influences solvent decomposition and hence, gas formation.

It is the purpose of this paper to investigate the effect of the Mn-ion oxidation state on PC decomposition and CO₂ gas generation. To accomplish this cyclic voltammetry and gas chromatography were used.

2. Experimental

Three different oxidation states of the Mn-ion were investigated: Mn⁴⁺ (MnO₂), Mn³⁺ (Mn₂O₃) and Mn²⁺ (MnO). Electrolytic manganese dioxide (EMD) was obtained from ChemMetals, The % of Mn⁴⁺ in MnO₂ was about 93% [14]. MnO (99% Mn²⁺) and Mn₂O₃ (99% Mn³⁺) were obtained from the Aldrich Chemical Company, X-ray diffraction confirmed that all three oxides were single phase. The structure of the EMD was single phase γ . EMD was given a standard commercial heat-

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treatment prior to use which involved heating it in air at 375°C for 24 h, followed by heating at 300°C under vacuum for 4 h [3]. X-ray diffraction revealed after the first heat-treatment a mixture of γ and β phases. No new phases were observed after the second heat-treatment. After the heat-treatment the structure of the MnO_2 used in this investigation was identical to the MnO_2 used by Bluestar in their Li/MnO_2 pouch cell batteries [15]. The MnO and Mn_2O_3 powders were used as received. The specific surface area of the three oxide powders was measured by the Brunauer, Emmett and Teller (BET) technique using nitrogen.

Propylene carbonate was chosen as the solvent since, it is the most widely used solvent in the Li/MnO_2 system [1,3,4,6–12]. The oxidative decomposition of PC as a function of the Mn-ion oxidation state was examined by recording linear voltammetric sweeps at room temperature in glass cells using an EG&G PAR potentiostat/galvanostat controlled by Model 270 software. The three-electrode configuration was used. The counter and reference electrodes were metallic lithium. The working electrode consisted of MnO_2 or Mn_2O_3 or MnO mixed with 5% polyvinylidene difluoride. This mixture was placed inside a cavity within a glassy carbon rod covered with shrinkable Teflon so only the oxide and binder powders were exposed to the electrolyte. The same weight of oxide and binder was used for all experiments. The scans were carried out between the open-circuit potential (≈ 3.2 – 3.6 V vs. Li/Li^+) and 5.0 V. The scan rate was 4 mV/s. The electrolyte consisted of a 1-M LiClO_4 : PC solution. LiClO_4 (Aldrich Chemical) was dried overnight at 130°C under vacuum prior to use. Propylene carbonate (Grant Chemical) was dried over 4-Å molecular sieves and verified by Karl–Fischer coulometric titration to have a moisture concentration of about 25 ppm. All work was carried out in a glove box with an argon atmosphere continuously monitored to be less than 0.5 ppm moisture/oxygen.

The amount of gas generated from PC decomposition for each Mn-ion oxidation state was determined by mixing a like amount (1 g) of MnO_2 or Mn_2O_3 or MnO powder with PC (1 g) in glass vials in a glove box. The vials were sealed and placed within a furnace for a period of 7 days held at 60°C. The vials were heated at 60°C to accelerate PC decomposition.

The presence and amount of CO_2 was determined with a Hewlett-Packard 5890 gas chromatography using helium as the carrier and reference gas. Gas samples were extracted from the vials with a gas tight syringe using the headspace sampling technique. The amount of CO_2 was determined using calibrated gas standards.

3. Results and discussion

Fig. 1 shows the current–potential curves for the electrochemical oxidation of PC containing 1 M LiClO_4 on

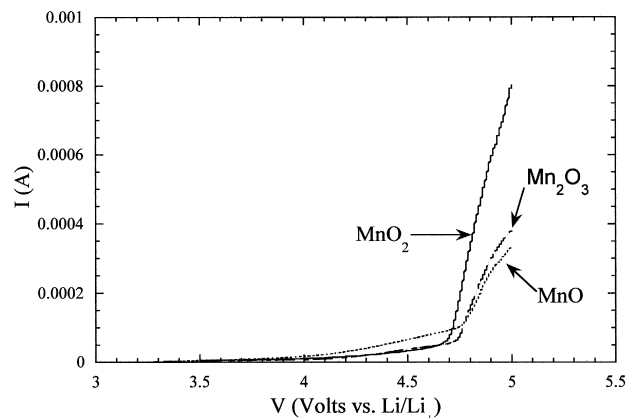


Fig. 1. Current versus potential curves for the anodic oxidation of propylene carbonate containing 1 M LiClO_4 on MnO_2 , Mn_2O_3 and MnO .

MnO , Mn_2O_3 and MnO_2 scanned from the open-circuit potential for each oxide till 5.0 V. The open-circuit voltage for $\text{MnO} = 3.37$ V, $\text{Mn}_2\text{O}_3 = 3.22$ V and $\text{MnO}_2 = 3.51$ V vs. Li/Li^+ . From Fig. 1 two important points are noted. Firstly, it can be observed that there is a rapid increase in current around 4.7 V for the three oxides. This rapid increase in current can be ascribed to bulk oxidation of PC. Additional testing revealed that the bulk oxidation voltage for PC containing 1 M LiClO_4 on $\text{LiMn}_2\text{O}_4(\text{Mn}^{3.5+})$ is 4.74 V and $\lambda\text{-MnO}_2(\text{Mn}^{4+})$ is 4.65 V [16]. $\lambda\text{-MnO}_2$ was synthesized by acid treatment of LiMn_2O_4 . The bulk oxidation for PC containing 1 M LiClO_4 as a function of the Mn-ion oxidation state is shown in Fig. 2. In addition, a line at $V = 4.70$ is also shown. From Fig. 2 it can be observed that bulk oxidation of PC is independent of the Mn-ion oxidation, with an oxidation voltage of about 4.70 V. This result is in contrast to suggestions in the literature [8], who propose that the oxidation of PC is a function of the Mn-ion oxidation state.

Secondly, from Fig. 1 it is observed that the value of the oxidation current at 5.0 V for $\text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{MnO}$. There are several possible explanations for this. These include; differences in particle surface area and/or water content. For example, it has been observed that as the particle surface area increases the amount of solvent decomposition increases (i.e., the magnitude of the oxidation current increases) [17]. BET surface areas for MnO_2 ranged from 26 to 33 m^2/g , for Mn_2O_3 from 2 to 3 m^2/g and MnO from 1 to 2 m^2/g . Thus, if the difference in the oxidation current is a result only of the difference in particle surface area, it would be expected that the oxidation current for $\text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{MnO}$. This prediction is in agreement with the results shown in Fig. 1. Hence, it is possible that the difference in the magnitude of the oxidation current is a result of the difference in the surface area for the various manganese oxides. However, it is also possible that the variation in the magnitude of the oxidation current shown in Fig. 1 is a result of a difference in water content.

It has recently been shown that an increase in water content in the electrolyte resulted in: (i) an increased oxidation current density, (ii) enhanced rate of CO_2 formation and (iii) no change in the potential where bulk oxidation began for 0.5 M LiClO_4 :PC on platinum [18]. Since, the amount of water in the electrolyte used for MnO , Mn_2O_3 and MnO_2 , was the same in all cases (25 ppm) this cannot explain the difference in the oxidation currents. However, there is another source of water which may be able to account for the difference in oxidation currents that is, the absorbed water on the oxide particle surfaces. To determine if absorbed water can account for the difference in the oxidation currents for MnO , Mn_2O_3 and MnO_2 , the absorbed water content of these oxides was determined from the change in weight before and after heating the oxide powders at 130°C under vacuum for 24 h. For the MnO_2 powders their absorbed water content, determined using the 130°C heat-treatment, was conducted after the two-stage commercial heat-treatment described in the experimental section. The absorbed water content is ≈ 0.4 wt.% for MnO_2 , ≈ 0.05 wt.% for Mn_2O_3 and ≈ 0.03 wt.% for MnO . Thus, if the difference in the oxidation current is a result only of the difference in the absorbed water content, it would be expected that the oxidation current for $\text{MnO}_2 > \text{Mn}_2\text{O}_3 > \text{MnO}$. This prediction is in agreement with the results shown in Fig. 1. Hence, it is possible that the difference in the magnitude of the oxidation current is a result of the difference in the absorbed water content for the various manganese oxides. It can be seen that both the particle surface area and water content predictions are in agreement with the experimental results. However, at present it cannot be determined which one (i.e., particle surface area or water content) of the two is dominating the oxidation current behavior or if they both acting together, which is probably the more likely case. This will be investigated in the future.

To confirm the cyclic voltammetry results, which suggest that PC decomposition is independent of the Mn-ion oxidation state gas chromatography studies were con-

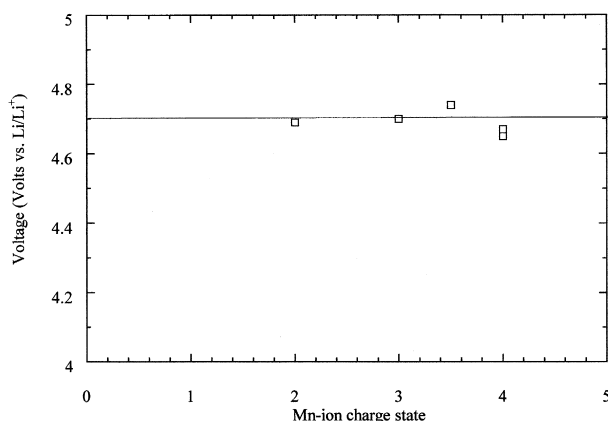


Fig. 2. Bulk oxidation voltage for propylene carbonate containing 1 M LiClO_4 as a function of the manganese-ion oxidation state.

Table 1

Gas species and quantity
PC = Propylene carbonate.

Reactants	Gas	Quantity (ppm)
PC	None	
PC + MnO	CO_2	114 ± 17
PC + Mn_2O_3	CO_2	120 ± 15
PC + MnO_2	CO_2	184 ± 22

ducted. The gases evolved and amount after 1 week at 60°C are listed in Table 1. From Table 1, several important points are noted. Firstly, it is observed that no gas was evolved for the case of only PC. Secondly, CO_2 is observed for all three-manganese oxides. No other gas was detected. This result: (i) confirms the literature suggestions [8,11–13] that CO_2 is the major gas associated with decomposition of PC and (ii) reveals that CO_2 gas is evolved for all Mn-ion oxidation states. Thirdly, the amount of evolved CO_2 gas is: (i) about the same for the Mn^{2+} (MnO) and Mn^{3+} (Mn_2O_3) oxidation states and (ii) highest for Mn^{4+} (MnO_2). These results are in close agreement with the oxidation current data shown in Fig. 1, in that a much higher current is observed for MnO_2 compared to Mn_2O_3 and MnO . It is likely that the larger quantity of CO_2 gas evolved on MnO_2 compared to Mn_2O_3 and MnO is related to its higher particle surface area and/or absorbed water content rather than the difference in the Mn-ion oxidation since, Mn_2O_3 (Mn^{3+}) and MnO (Mn^{2+}) of about the same particle surface area and absorbed water content both evolved about the same amount of evolved CO_2 gas. It would be expected that if the Mn-ion oxidation state affected the amount of evolved CO_2 gas, a significant difference in the amount of gas between MnO and Mn_2O_3 would be exhibited, whereas none was observed. Hence, the gas chromatography results tend to support the cyclic voltammetry results, that PC oxidation is independent of the Mn-ion oxidation state.

4. Conclusions

Cyclic voltammetry revealed that the oxidation voltage of propylene carbonate (PC) containing 1 M LiClO_4 on MnO , Mn_2O_3 and MnO_2 is approximately 4.7 V. This result suggests that the oxidation of PC is independent of the Mn-ion oxidation state, in contrast to suggestions in the literature. The difference in the magnitude of the oxidation current for MnO , Mn_2O_3 and MnO_2 is most likely a result of the difference in particle surface area and/or absorbed water content between the various manganese oxides. Gas chromatography results tend to support the voltammetry results, that PC oxidation is independent of the Mn-ion oxidation state. CO_2 is the major gas evolved from the decomposition of PC on MnO , Mn_2O_3 and MnO_2 . The amount of CO_2 from the decomposition of PC on MnO

and Mn_2O_3 , of about the same particle surface area and absorbed water content, is about the same. The larger amount of CO_2 gas evolved on MnO_2 compared to Mn_2O_3 and MnO is most likely related to its higher particle surface area and/or absorbed water rather than a difference in the Mn-ion oxidation state. An important consequence of this study is that reducing the oxidation state of the Mn-ion does not eliminate completely CO_2 gas formation in the Li/ MnO_2 system and hence, may not eliminate swelling of the pouch cells that contain PC as component of the electrolyte.

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