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## Development of electrolyte inhibitors in nickel cadmium batteries



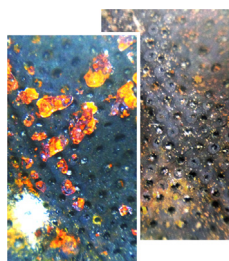
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## HIGHLIGHTS

- Novel inhibitors were developed to retard CO<sub>2</sub> absorption in alkaline electrolytes.
- The kinetics parameters and mechanism of CO<sub>2</sub> absorption inhibitors were justified.
- The types and concentrations of CO<sub>2</sub> absorption inhibitors were optimized.
- CO<sub>2</sub> inhibition resulted in improvement of battery capacity and lifetime.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The aim of this project was enhancement the stability of alkaline electrolyte in nickel cadmium batteries during unavoidable gradually CO<sub>2</sub> absorption from the air. As the most concern of nickel cadmium batteries, CO<sub>2</sub> absorption intensifies the electrolyte damage *via* diverting the hydroxide to the carbonate anions leading to depletion of battery capacity and electrical performance. The objectives of this paper are (1) investigation of novel chemical inhibitors to retard the deleterious CO<sub>2</sub> absorption in alkaline electrolytes and (2) development of kinetics and mechanisms to justify their behavior. Some homologues of CO<sub>2</sub> absorption inhibitors were experimentally examined at different levels and their reaction kinetics and experimental characteristics were determined. The results revealed that low dosages of such inhibitors in alkaline electrolyte of nickel cadmium batteries declines CO<sub>2</sub> absorption and hydroxide consumption (or carbonate formation) and increases the lifetime of both electrolyte and electrodes. The experimental achievements were applied in some blocks of industrial nickel cadmium batteries representing a fantastic inhibition of CO<sub>2</sub> absorption in alkaline electrolyte.

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## 1. Introduction

The first patent on nickel cadmium batteries was awarded to W. Jungner in 1899 who invented one of the alkaline batteries referred to as Ni-Cd cell (Shukla et al., 2009). The main problem of alkaline electrolyte batteries, which has been reported since 1930 s, is electrolyte degradation and reducing the battery capacitance and lifetime. Nickel cadmium batteries suffer from carbon dioxide absorption from the air during the time. The alkaline electrolyte in these batteries absorbs carbon dioxide as an air component (about 400 ppm) or as an added water impurity (Hauel, 1939) and is changed from hydroxide- to carbonate-solution. There are other factors with fewer effects on the battery

efficiency including the electrochemical and chemical degradation of nylon separator, located between anode and cathode plates (Lira et al., 1989).

The alkaline electrolyte of nickel cadmium batteries consists of aqueous solutions of potassium hydroxide (KOH) as the main component and lithium hydroxide (LiOH) as an additive. Depending on the relative concentration of LiOH with respect to KOH (31% wt. or 6.0 M), there are a series of alkaline electrolytes named as E1 (0.4% wt. LiOH), E12 (1.2% wt. LiOH), E13 (1.3% wt. LiOH), E21 (2.1% wt. LiOH), E22 (2.0% wt. LiOH), E30 (3.0% wt. LiOH). The manufactures advise to use alkaline electrolytes E22 and E13 in the time of battery instillation and regeneration, respectively (Electrolyte, 2004).

**Table 1**  
Electrical conductivity for carbonate and hydroxide ions at different concentrations (Wolf, 1966; Weast, 1989).

Dissolved Salt	Salt Concentration (% wt.)			
	0.5	1.0	2.0	5.0
KOH	20.0	38.5	75.0	178
K <sub>2</sub> CO <sub>3</sub>	7.0	13.6	25.4	58.0

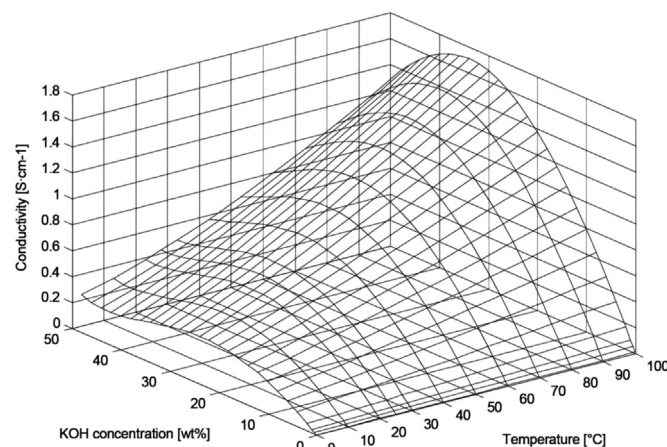
The electrical conductivity for carbonate and hydroxide ions at different concentrations of 0.5%, 1.0%, 2.0% and 5.0% wt. are presented in Table 1 (Wolf, 1966; Weast, 1989). The conductivity of product solution (more carbonate and less hydroxide) is less than that of the source solution (less carbonate and more hydroxide). Therefore, the manufacturers of nickel-cadmium batteries often specify to replace the alkaline electrolytes once annually. It has been reported that each 5 h discharge leads to form carbonate ions (9% wt.) in electrolyte (Hauel, 1939) with no sensible effect on the battery performance. This level of carbonate in the electrolyte is assumed the maximum acceptable level and more than it the electrolyte should be replaces.

It has been claimed that reduction of battery efficiency (due to carbonate formation or hydroxide consumption of electrolyte) is attributed to current failure of negative electrode rather than that of positive electrode. Carbonate ions in cell electrolytes form a poor-conducting film of cadmium carbonate deposited on the surfaces of fine-grained cadmium oxide and it is removed after replacement of the spent electrolyte. Eqs.(1)–(3) depict the reaction of carbon dioxide and alkaline electrolyte to yields carbonate ions (Gondal et al., 2015).



The equilibrium presented as Eq.(1) represents the physical dissolution of gaseous carbon dioxide in aqueous phase which is described by the Henry's law (Pohorecki and Moniuk, 1988). The reaction depicted as Eq.(2) shows the hydration of dissolved carbon dioxide in aqueous phase, which controls the overall rate of reaction (Pohorecki and Moniuk, 1988; Thee et al., 2012; Knuutila et al., 2010; Astarita, 1963; Astarita et al., 1981; Pohorecki, 1976; Barrett, 1966; Nijssing et al., 1959; Himmelblau and Babb, 1958; Pinsent and Roughton, 1951; Pinsent et al., 1956). Some researchers have claimed that Eq.(2) is a second-order reaction composed of two first-order reactions with respect to hydroxide and carbon dioxide (Pohorecki and Moniuk, 1988; Knuutila et al., 2010; Hikita et al., 1976; Haubrock et al., 2007), while it is revealed that this simple mechanism is just a simplified form of the main complex state.

Halpert and May (1977) investigated the open circuit potential of batteries in different KOH concentrations from 10% to 40% wt. Allebrod et al. (2011) reported the results of cell conductivity ( $\sigma$ ) with respect to electrolyte concentration of KOH solutions (Fig. 1). Therefore, sensing the electrical conductivity of electrolyte is a practical way to determine the KOH concentration or the electrolyte consumption of a battery cell rather than titration of



**Fig. 1.** The solutions conductivity of KOH electrolytes (Allebrod et al., 2011).

alkalinity tests. In the present study, the conductivity monitoring was followed up to study the inhibition role of carbon dioxide in battery performance.

See and White (1997) investigated the KOH electrolyte in the range of 0–100 °C and in the concentrations up to 45% wt. Gilliam et al. (2007) reported the KOH electrolyte in temperature and concentration ranges of 0–100 °C and 0–48% wt, respectively. The temperatures and concentrations of KOH electrolyte up to 200 °C and 37.5% wt. were examined by Lown and Thirsk (1971). Likewise, the temperatures and concentrations of KOH electrolyte up to 260 °C and 45% wt. were examined by Yushkevich et al. (1967).

Absorptions and dissolution of carbon dioxide as an acid gas in carbonate-base electrolytes can be inhibited chemically (Spigarelli and Kawatra, 2013). In this research, some carboxylic acid salts were added to KOH electrolytes exposed to carbon dioxide and the results revealed that absorption of carbon dioxide was inhibited significantly. Format, acetate and propionate salts were examined as inhibitor ( $\text{In}^-$ ) additives in concentration of 0.1% wt. to postpone the electrolyte damage during the time or increase the lifetime of nickel cadmium electrodes. This paper has presented the experimental results dealing with how a proper  $\text{In}^-$  can increase the battery efficiency. The side-effects of such additives on the electrodes lifetime were briefly assessed; however, more subjects can be investigated in the upcoming works.

## 2. Experimental methods

The present study was performed by determining the degree of spent KOH electrolyte in the industrial batteries as well as predicting the effect of inhibited electrolyte on CO<sub>2</sub> absorption and KOH neutralization in the tested electrolyte.

### 2.1. Sampling and electrolyte specification

An industrial battery-room containing more than 6000 cells of nickel cadmium battery as 1500 blocks was assessed in the experiments. The battery cells were purchased from Saft Nife Company and their types were SBL 1020-1, SBM 161-2, SBM 203-2, SBL 214-2, SBL 995-1 and L 324-1. The concentrations of KOH and K<sub>2</sub>CO<sub>3</sub> in each series of cells (10 blocks or 40 cells) were determined by electrical conductivity and alkalinity test titration (ASTM D1067 and D3875). Fig. 2 shows a photograph of some series of cells and sampling procedure from the 2nd cell of the 10th block.

Matrices A and B show the concentration of KOH and K<sub>2</sub>CO<sub>3</sub> in the above mentioned series of cells (10 blocks or 40 cells),

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