Experimental and theoretical investigation of γ-butyrolactone decomposition on lithium electrode surface. Effect of Li₃N layer


Institute of Problems of Chemical Physics of the Russian Academy of Sciences, I ppros. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax.: +7 (496) 522 5625. E-mail: oyarm@icp.ac.ru

Dependence of gassing upon decomposition of 1 M LiClO₄ electrolyte in γ-butyrolactone (γBL) with various contents of water (0.008 and 0.2% w/w) at a lithium electrode on the current density of charging was studied. Quantum chemical modeling of γBL interaction with lithium surface was performed. The initial stage of γBL decomposition is the formation of a surface organolithium compound, which is hydrolyzed in the subsequent reactions with water.

Key words: γ-butyrolactone, lithium electrode, lithium nitride, gassing, quantum chemical modeling, density functional theory.

Lithium batteries are fairly promising electrochemical power sources. However, there is a number of problems brought about by deterioration of the lithium—electrolyte interface with time. First, cycling in organic electrolytes is accompanied by side corrosion reactions of lithium metal and decomposition of electrolyte components to give gaseous products, which increase the pressure inside the electrochemical cell. Second, dendrite formation creates conditions for short-circuit failure on the lithium electrode surface.

The problem of passivation of the lithium electrode surface in organic electrolytes has been known since the 1970s.¹ Thermodynamic calculations indicate that lithium reduces aprotic polar solvents used in lithium batteries.² For a number of solvents (ethylene carbonate, propylene carbonate, ethyl methyl carbonate, dimethyl carbonate, etc.), the reactions with lithium and the composition of the surface layers have been studied rather comprehensively.²,³ On going from pure solvents to electrolytes, the electrolyte salt also becomes involved in the construction of surface layers together with the solvents.²,³ Only some compounds do form a surface layer on lithium in different solvents and electrolyte solutions. The inorganic compounds that refer to this type include the oxide Li₂O, hydroxide LiOH, carbonate Li₂CO₃, chloride LiCl, fluoride LiF, dithionite Li₂S₂O₄, carbide Li₂C, and nitride Li₃N. Among organic compounds, lithium methoxide and butoxide with the formula ROLi should be mentioned.²,³ Electrolyte decomposition processes and compositions of the surface layers have been studied in a number of works.⁴—¹⁹

On lithium contact with many gases (including dry O₂ and CO₂), organic and inorganic solvents, and solutions on the metal surface, a passive protective film is formed, representing a layer of insoluble products formed in the reaction of lithium with the environment.²⁰ This is a continuous, non-porous, 1—100-nm thick layer having low electronic conductivity, which retards the redox processes involving the electrolyte. Meanwhile, the formation of the insulating layer does not deprive lithium of the electrochemical activity. While functioning as the negative electrode in contact with an electrolyte, lithium is dissolved at a rather high rate (at a current density of up to 0.1 and even 0.5—1.0 mA cm⁻²) without disruption of the passive layer. Hence, the layer material possesses electrical conductivity of lithium ions, thus functioning as a lithium-conducting ionic conductor or solid electrolyte.

The purpose of this work is experimental and theoretical study of γ-butyrolactone (γBL) decomposition on the surface of a lithium electrode during charging with lithium electrode potential shift to negative region. The reaction of γBL with alkali metals was studied previously.²,³ It is known² that lithium cutting under a γBL layer produces a short gas pulse after which the surface is passivated; however, gas release on sodium or potassium is more prolonged. The gases were found² to contain methane and C₂, C₃, and C₄ hydrocarbons. In the absence of gassing in moist γBL, the salt LiO(CH₂)₃COOLi was found.³ The effect of coating the lithium electrode by a thin layer of lithium nitride, which functions as ionic conduc-
tor with a conductivity of \((2—4) \cdot 10^{-4} \text{ Cm cm}^{-1}\) at 20 °C, on the decomposition of 1 \(M\) LiClO\(_4\) electrolyte in \(γBL\) in the presence of 0.2% (w/w) water was studied.\(^{21}\)

Studies of the composition and formation mechanism of the gaseous products in the reaction of the lithium electrode surface with 1 \(M\) LiClO\(_4\) in \(γBL\) in the presence of water is of considerable practical value, as the manufacturers of lithium ion batteries are always faced with the problem of unsuitability of a wet electrolyte.

**Experimental**

A 1 \(M\) LiClO\(_4\) electrolyte in \(γBL\) (LLC Ecotech, Chernogolovka) with a water content of 0.008% (w/w) was used. The side electrolyte decomposition reactions were studied by introducing 0.2% (w/w) of water.

Lithium electrodes were manufactured using a 120 μm Ni grid (inert toward the electrolyte studied). A 2-mm thick lithium metal foil was pressed onto the grid; the surface area was 1 cm\(^2\). All operations with lithium metal were carried out in an argon glove box.

To obtain the lithium nitride coating, a lithium electrode was placed in an ampoule and evacuated, and high-purity nitrogen was let in under atmospheric pressure. The ampoule with the lithium electrode in a nitrogen atmosphere was kept at 100 °C until a black-colored coating appeared on the lithium surface (2—4 h).

To determine the amount of nitrogen on the surface, the lithium electrode was dissolved in 0.1 \(M\) HCl (special purity grade). The ammonium salts thus formed were converted to ammonia on refluxing in 40% alkali, the ammonia being steam-distilled off into 0.01 mol acid, and this solution was analyzed by means of phenol and sodium hypochlorite (indophenol method of nitrogen analysis).\(^{22}\) The nitrogen content in the lithium surface layer was \(7.8 \cdot 10^{-4}\) mol, which corresponds to a 0.125-mm thick lithium nitride layer.

The release of gaseous products of 1 \(M\) LiClO\(_4\) electrolyte decomposition in \(γBL\) was studied in the galvanostatic mode on a P-5827 \(М\) potentiostat at a current density of 0.5, 1.0, 1.5, and 2.0 mA cm\(^{-2}\) in a three-electrode cell (Fig. 1) at 20 °C. A standard silver chloride electrode was used as the reference electrode; it was separated from the electrolyte by an electrolytic bridge filled with the same electrolyte. Platinum metal served as the counter electrode. The cell was connected to a vacuum circulation setup with argon (special purity grade) being continuously pumped through the closed circuit during the electrolysis. The argon pressure in the setup was higher than atmospheric pressure by \(\approx 10\) Torr in order to avoid air inflow from the atmosphere. The contents and the composition of the hydrocarbons evolved during the electrolysis were analyzed by taking samples by means of the multiway valve, the samples being supplied to a Biokhrom chromatograph with \(Al_2O_3\)-packed columns (0.4×300 cm) and a flame ionization detector.

The gas phase was additionally analyzed by mass spectrometry to determine the content of hydrogen and oxygen compounds. Mass spectrometric analysis was carried out using a MI 1201V mass spectrometer. The gas phase was sampled at the end of the experiment.

**Results and Discussion**

Gasification as a result of decomposition of wet 1 \(M\) LiClO\(_4\) electrolyte in \(γBL\) was studied in the galvanostatic mode. This electrolyte with a water content of 0.008% w/w does not decompose at a pure lithium electrode even when the current density increases to 2.0 mA cm\(^{-2}\).

At a pure lithium electrode and current densities of 0.5 and 1.0 mA cm\(^{-2}\), \(γBL\) does not decompose in the presence of 0.2 mol.% of water, while at current densities of 1.5 and 2.0 mA cm\(^{-2}\), five gaseous hydrocarbons are evolved, the release rate and the product ratio being varied upon change in the current density (Fig. 2). The products include both saturated \((C_3H_8, C_2H_6, CH_4)\) and unsaturated hydrocarbons \((C_3H_6, C_2H_4)\) but no \(C_4\) hydrocarbons.

When the current density is 1.5 mA cm\(^{-2}\), ethane is the major product of electrolysis, the yields of other products increasing in the sequence \(\text{CH}_4 < C_3\text{H}_6 < C_3\text{H}_8 < C_2\text{H}_4 < C_2\text{H}_6 < C_3\text{H}_8\) (Table 1, see Fig. 2). For a current density of 2.0 mA cm\(^{-2}\), the initial rates of hydrocarbon formation increase 1.5—6.6-fold and a different product ratio is observed, namely.: \(\text{CH}_4 < C_3\text{H}_6 < C_3\text{H}_8 < C_2\text{H}_4 < C_2\text{H}_6 < C_3\text{H}_8\). Changes in the product yields are much more pronounced than the increase in the current density, indicating a considerable effect of electrochemical processes. Moreover, the properties of the lithium surface change with time at a constant current density (1.5 mA cm\(^{-2}\)), as follows from the kink on the kinetic curve of ethylene formation. Note that the experiments were carried out at one and the same electrode with successive increase in the current density.