

LEAD OXIDES AS CATHODE MATERIALS FOR VOLTAGE-COMPATIBLE LITHIUM CELLS

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Summary

Yellow β -PbO (massicot) and β -PbO₂ (plattnerite) have been investigated as cathode materials in organic electrolyte lithium cells. The main characteristics and performance of these cells have been examined and the discharge mechanism discussed on the basis of X-ray data. The two oxides are particularly interesting as candidates for voltage-compatible lithium cells. They exhibit long voltage plateaux of appropriate values and appreciable specific capacities and energies.

1. Introduction

Recently, attention has been focused on organic electrolyte primary lithium cells having a working voltage in a range (1.2 - 1.5 V) close to that of conventional systems. These, so-called, "voltage-compatible" lithium cells are thus expected to be interchangeable with conventional primary cells such as Zn/MnO₂ and Zn/HgO cells, with little modification of existing equipment. Only two types of these batteries have reached the commercial stage: Li/CuO [1] and Li/FeS [2].

Research is currently underway to investigate the electrochemical characteristics of various positive electrode materials to be employed in this new class of lithium cells.

The use of lithium as an anode offers many performance advantages over conventional cells. Firstly, a substantial increase in energy density and, secondly, of equal importance, a long shelf life which presents the opportunity for new applications. Hence, the application of lithium cells is foreseen in fields having a rapid technological development such as the power

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supply for miniaturized electronic instrumentation (electronic watches, computers, displays, robots, etc.).

Different cathodic materials have been considered, particularly copper compounds [1, 3, 4] as well as lead [5, 6] and bismuth [7] oxides. In respect of the lead oxides, PbO and PbO₂ [5] have also been examined; however, a complete investigation was mainly undertaken on the performance of Pb₃O₄ and Bi₂Pb₂O₅ [5, 6], which have proved to be useful in miniature lithium cells with a working voltage similar to that of silver oxide-zinc cells [6].

Within a research programme on the behaviour of metal oxides in non-aqueous lithium cells [8, 9], and with the aim of increasing the basic knowledge on lead oxides, yellow PbO (massicot) and PbO₂ (plattnerite) have been examined as possible alternative materials in "voltage-compatible" lithium cells.

2. Experimental

Yellow orthorhombic (C_{2v}^8 space group) β -PbO (massicot) from two different origins was studied; a 99.5% pure Carlo Erba product and a high-purity (99.999%) Aldrich Chemical Company product. The tetragonal (D_{4h}^{14} space group) β -PbO₂ (plattnerite) was a 99% pure Merck product. The composition and structure of the oxides were checked by X-ray diffraction analysis using monochromatic Cu K α radiation. X-ray diffraction analysis was also employed for the identification of the discharge products obtained during the electrochemical investigations.

ESCA measurements were made in both FRR (Fixed Retard Ratio) and FAT (Fixed Analyser Transmission) modes. Al K α (1486.6 eV) unmonochromatized radiation was used as the exciting source. Calibration of the kinetic energy scale was *versus* the silver Ag3d_{5/2} signal (1118.7 eV) and correction of the kinetic energy values for sample charging was made on the basis of the carbon C1s peak (1202.0 eV) present due to surface contamination. Measurements were carried out at a pressure of about 10⁻⁹ Torr. The spectra were collected using a microcomputer, and stored as a series of datafiles on floppy disk. A second computer was used for data analysis with the following options [10]: smoothing, non-linear background subtraction, radiation satellites subtraction, peak area measurement, curve synthesis by using a mixed Gaussian/Lorentzian peak shape. The bands used in fitting the peak envelope were defined by their centroid position, half-width at half maximum, and peak height.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were also performed. The typical heating rate was 10 °C min⁻¹ and the purge gas was dry and oxygen-free nitrogen.

Electrochemical measurements were carried out using standard equipment, with two-electrode cells, as already described [8].

The lithium disc electrode of 12 mm dia. was a high purity (more than 99.9%) Alfa Ventron product. The reduced copper powder (99%) used as a substrate for the oxide pellets was supplied by Carlo Erba.

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Four different electrolytes were tested: 1 M LiClO_4 -propylene carbonate (PC); 1 M LiAsF_6 - γ -butyrolactone (BL), 1 M LiCF_3SO_3 -BL and 0.5 M LiCF_3SO_3 -PC. To purify the solvents and the salts, the procedures previously reported were followed [8].

In addition to galvanostatic discharge curves at various current densities, step polarization tests were also performed. The cell was submitted to a sequence of galvanostatic pulses at increasing current densities for a fixed period (typically 30 s) and the corresponding voltages were recorded. After each pulse the circuit was opened for the time necessary to reach quasi steady-state conditions (usually 30 s).

3. Results and discussion

3.1. X-ray analysis

The X-ray powder spectra of the three powders contained all of the reflections reported in the ICPDS 5-0570 and ICPDS 25-0447 cards for β -PbO and β -PbO₂, respectively. The spectrum of the Carlo Erba PbO, however, contained some additional diffraction peaks of uncertain origin, though probably attributable to PbO₂ on the basis of ESCA results, as discussed below.

3.2. Thermogravimetric analysis and differential scanning calorimetry

The TGA curve of β -PbO (Aldrich) up to a temperature of 480 °C did not show any measurable weight loss, and no isothermal heat exchange was observed in the DSC curve. The baseline slope, however, slightly increased, particularly at higher temperatures, owing to changes in the specific heat. No structural change was observed in the considered temperature range (the polymorphic conversion between the yellow (orthorhombic) and the red (tetragonal) lead oxide takes place at 489 °C [11a]). It is worth noting, however, that, in our experience, the heat involved during solid state phase transitions (of tungsten and molybdenum trioxides [9], for example) is usually so small as not to be noticed in the DSC curve unless particular precautions are taken, even though the final product has a new crystalline structure.

Typical TGA and DSC curves of PbO₂ are reported in Fig. 1. The TGA results indicate that most of the observed weight loss takes place below 600 °C associated with broad endothermic bands in the DSC curve. At the end of the experiments, X-ray diffraction analysis showed the material to be a mixture of yellow and red PbO. Hence, the endothermic reaction is related to the thermal instability of PbO₂. According to published data, PbO₂ decomposes on heating in air, beginning at 280 - 300 °C, and forming, successively, the following lower, nonstoichiometric oxides: PbO₂ (290 - 320 °C) \rightarrow Pb₂O₃ (390 - 420 °C) \rightarrow Pb₃O₄ (530 - 550 °C) \rightarrow PbO [11b]. In nitrogen, however, PbO₂ gives rise to three endothermic effects: loss of sorbed water at about 100 °C, formation of Pb₃O₄ at about 400 °C and of PbO at about 620 °C [12].

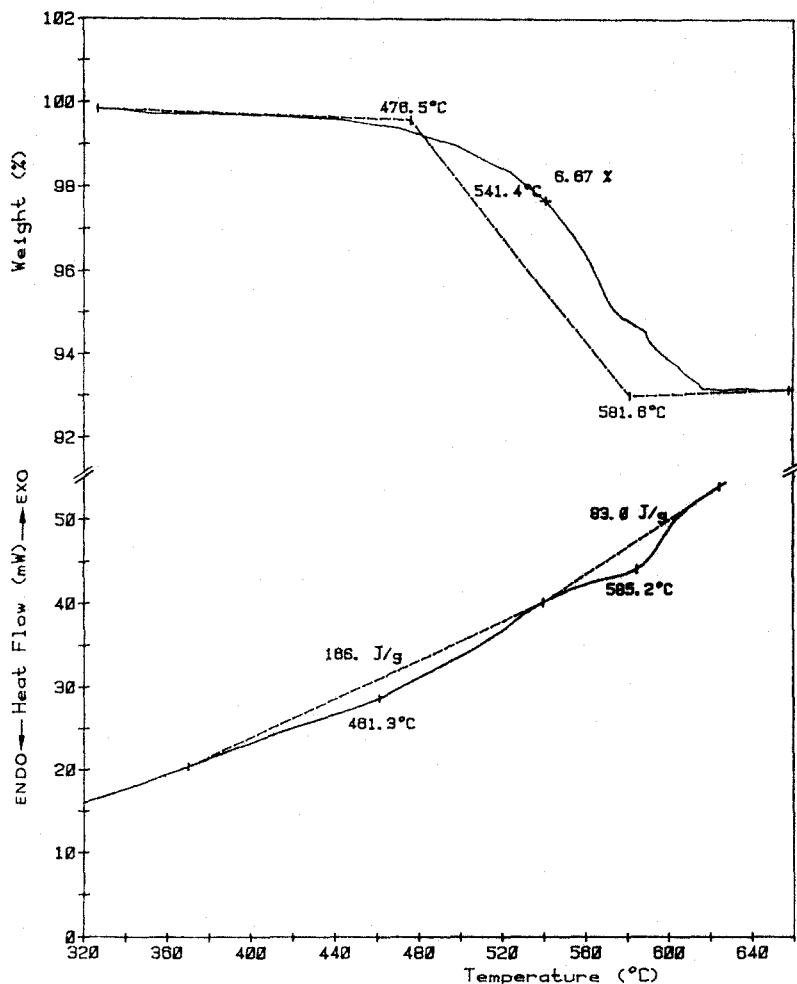


Fig. 1. Thermogravimetric analysis curve and differential calorimetry spectrum of PbO_2 .

Although the individual decomposition steps could not be recognized in our TGA and DSC curves (such an analysis was outside the scope of the work), the irregular trend of the weight loss and of the heat flow, as well as the wideness of the absorption band, are indicative of a complex interaction among the different possible reactions.

The total weight loss (6.67%) closely agrees with that theoretically calculated (6.69%) for the decomposition of PbO_2 to PbO , thus indicating a negligible water content in our material.

In respect of the heat exchanged, the standard heat of PbO_2 decomposition to PbO at 25 °C calculated from thermodynamic data [11c] is about $-250 \text{ J g}^{-1} \text{ PbO}_2$. This may be compared with the values shown in Fig. 1, which are -269 J g^{-1} .

3.3. Surface morphology

The surface morphology, as well as the surface area, the porosity, and the wettability of a cathode material to be used in lithium cells, play a very important role in determining its main properties and performance and were, therefore, characterized for the two oxides. Both particle shape and particle size contribute to the surface area of a cathode powder and, hence, scanning electron microscopy examinations and determinations according to the Brunauer, Emmett and Teller method [13] have been performed.

The PbO_2 powder presented a smoother surface than the PbO powder. The BET surface areas were 2.43 and $0.04 \text{ m}^2 \text{ g}^{-1}$ for PbO (Aldrich) and PbO_2 , respectively, while the pore volume was nearly the same (around $0.01 \text{ cm}^3 \text{ g}^{-1}$).

3.4. Electrochemical investigations

3.4.1. Discharge process

Cathodic pellets of both PbO and PbO_2 were obtained by compressing the powders at 350 MPa on an inert metallic (copper) support. The experiments were performed at ambient temperature in a two-electrode cell of the type:

(-) Li/electrolyte/lead oxides (+).

In agreement with our previous results on the porosity of the compounds, as well as with published data on the conductivity of lead oxides [11d, 14], preliminary measurements indicated that the performance of the materials cannot be improved by adding a binding agent (5% by weight powdered PTFE) and/or an electronically conductive agent (10% graphite).

Four electrolytes were tested in order to select the best results; 1 M LiClO_4 -propylene carbonate (PC), 0.5 M LiCF_3SO_3 -PC, 1 M LiAsF_6 - γ -butyrolactone (BL), and 1 M LiCF_3SO_3 -BL.

A great difference in behaviour was observed, particularly in the case of the higher valence oxide, PbO_2 . The LiClO_4 -PC electrolyte gave the most satisfactory result in terms of average voltage and discharge depth, and the BL-containing solutions the worst (Fig. 2). Consequently, the former electrolyte was chosen for the further development of the research and, as recently pointed out [15, 16], the LiClO_4 -PC solution seems to be particularly well tailored for lithium power sources.

The open circuit voltages of the Li/ PbO and Li/ PbO_2 cells were checked in a long-term (1 month) experiment and were found to be constant at about 3.1 and 3.3 V *versus* Li/Li^+ , respectively.

Typical discharge curves of these cells at various current densities are reported in Figs. 3 and 4, the composition parameter on the abscissa referring to lithium equivalents inserted into one mole of the oxide. The striking feature of the curves is the very long plateau at a voltage of around 1.3 V *versus* Li/Li^+ (at 0.5 mA cm^{-2}).

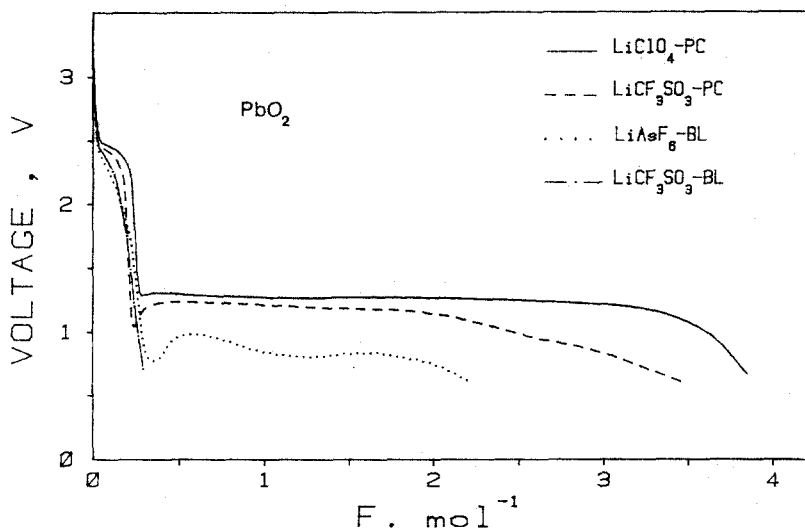


Fig. 2. Discharge curves of PbO_2 in various electrolytes at 0.5 mA cm^{-2} at room temperature.

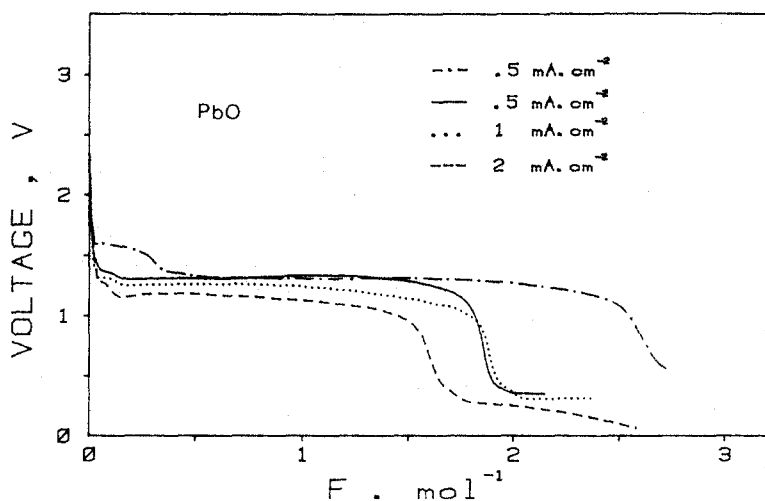


Fig. 3. Discharge curves of PbO (Aldrich) in $1 \text{ M LiClO}_4\text{-PC}$ at different current densities at room temperature. ---, refers to PbO (Carlo Erba) at 0.5 mA cm^{-2} .

At the end of the discharge process, X-ray diffraction peaks due to lead only were observed in the spectra of the materials, the peaks caused by the original lead oxide being no longer visible. Even though lithium oxide identification was impossible owing to the much smaller atomic scattering factors of lithium and oxygen in comparison with that of lead, it may be argued that the discharge process mainly consists of a displacement reaction where lead atoms are replaced by lithium atoms, *i.e.*,

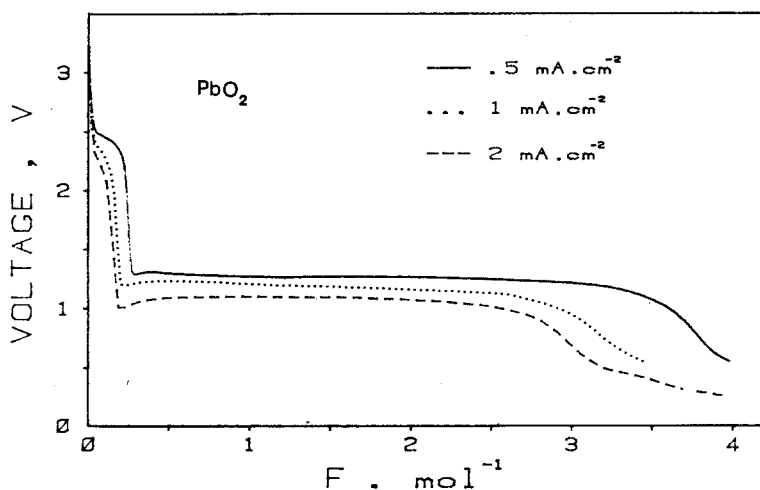
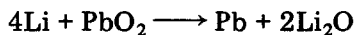


Fig. 4. Discharge curves of PbO_2 in 1 M LiClO_4 -PC at different current densities at room temperature.



in the case of the $\text{Li}/\text{LiClO}_4\text{-PC}/\text{PbO}$ system, and



in the case of the $\text{Li}/\text{LiClO}_4\text{-PC}/\text{PbO}_2$ system.

These results also agree with the discharge reactions approximately involving two and four Faraday per mole of PbO (Aldrich product) and PbO_2 , respectively.

As already noted for other lead oxides, *e.g.*, Pb_3O_4 [5, 6], $\text{PbO}_{1.5}$ and $\text{PbO}_{1.8}$ [5], the discharge process of the Li/PbO_2 couple seems not to occur in steps, namely, through a preliminary reduction step to lower valence oxides followed by a subsequent reduction step to lead. This is thermodynamically unexpected when one considers the potential of the various possible redox couples in neutral aqueous solutions [17]. Hence, kinetic factors have to be taken into account.

3.4.2. Initial spikes

The discharge curves of the two PbO samples having a different origin are compared in Fig 3. In the lowest purity material one observes the presence of a characteristic initial voltage drop followed by a very short quasi-plateau. Moreover, apparently more than two lithium equivalents per mole of PbO could be discharged, in contradiction to what is expected on the basis of the previously considered reduction reaction.

X-ray photoelectron spectroscopy analysis of the pellets showed that the 99.5% oxide contains a high quantity of PbO_2 to which the observed behaviour may be ascribed. The results are reported in Fig. 5, where the spectrum of the Pb 4f region is depicted. Each band of the spectrum was

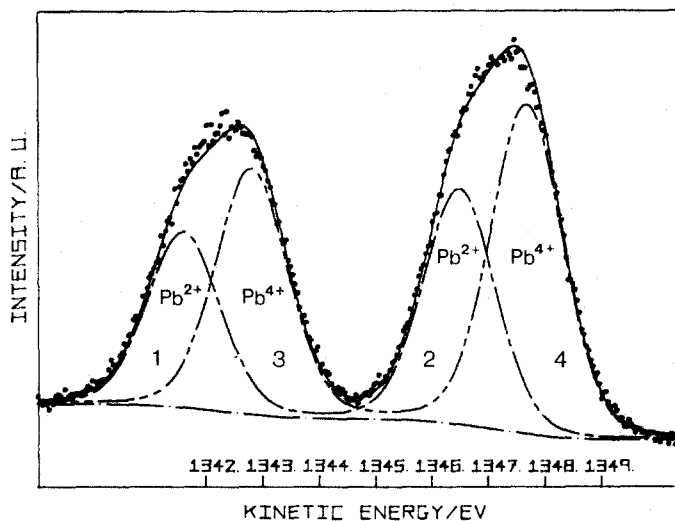


Fig. 5. ESCA spectra relevant to Pb 4f core level electrons recorded on the Carlo Erba PbO sample. Peaks 1 and 2 and peaks 3 and 4 are due to Pb^{2+} and to Pb^{4+} species, respectively. Kinetic energy values are not corrected for sample charging.

deconvoluted into two peaks. Those having the lower kinetic energy (peaks 1 and 2) are in agreement with the peaks expected for PbO , and those having the higher values (peaks 3 and 4) are due to PbO_2 [18, 19]. The ratio of the areas under the peaks gives a molar composition of the specimen surface equal to 42% PbO and 58% PbO_2 . Hence, as is often recognized [20], ESCA is an excellent technique for obtaining information on the chemical speciation of a surface and it complements the other techniques used which provide information about topology, morphology or elemental composition.

In consequence of these results, the hypothesis that lead could form compounds where it is in the negative oxidation state, as suggested, for example, for bismuth in $\text{Li}/\text{Bi}_2\text{O}_3$ cells [21] was ruled out. Moreover, the "so-called" 99.5% PbO was excluded from further research.

Particular interest was then shown in the initial voltage drop and the quasi-plateau occurring for low lithium insertion in PbO_2 (Fig. 4). This was to establish whether they could be related to the presence of traces of electrochemically reducible impurities not detectable by X-ray analysis, as the spectra of the pristine compound perfectly matched that reported in the ICPDS cards. This is an important aspect of performance since such initial spikes are not compatible with most practical applications.

Preliminary measurements in cells in which the oxide pellet was not supported by a copper substrate also showed these 'spikes' and, therefore, it is now thought that they cannot arise from the reduction of copper impurities.

Experiments were therefore undertaken in which a cell containing PbO_2 as the positive electrode was submitted to a shallow discharge up to

TABLE 1

Performance of lead oxides in a room temperature lithium cell at different current densities and in 1 M LiClO₄-PC (cut-off: 1 V)

Current density (mA cm ⁻²)	Mean discharge voltage (V)	Depth of discharge (F mol ⁻¹)	Sp. capacity (A h g ⁻¹)	Vol. capacity* (A h dm ⁻³)	Sp. energy (W h g ⁻¹)	Vol. energy* (W h dm ⁻³)
<i>PbO (Aldrich)</i>						
0.5	1.19	1.82	0.250	2.355	0.295	2.795
1	1.20	1.82	0.200	1.925	0.242	2.310
2	1.13	1.49	0.165	1.575	0.185	1.780
<i>PbO₂</i>						
0.5	1.27	3.58	0.370	3.475	0.475	4.435
1	1.16	2.89	0.310	2.890	0.360	3.370
2	1.07	2.55	0.265	2.465	0.280	2.640

*Assuming a density of 9.53 (PbO) and 9.375 (PbO₂) g cm⁻³ [11e].

about 0.17 F mol^{-1} , interrupting the discharge process just before the occurrence of the plateau at 1.3 V versus Li/Li^+ . ESCA investigation of the material after such partial discharge showed very strong peaks due to metallic lead, thus indicating that the displacement reaction takes place even at the very beginning of the discharge process.

Further studies in this area are currently underway.

3.4.3. Current density

The influence of the discharge rate on the cell characteristic was also investigated for the Li/PbO and Li/PbO_2 systems (Figs. 3 and 4, respectively). The gravimetric and volumetric specific capacity and energy for a cut-off voltage of 1 V are reported in Table 1, together with the mean discharge voltage and the depth of discharge at three different current densities. The data show the promising behaviour of the two materials, more especially of lead dioxide, which presents a high specific energy even at a current density of 2 mA cm^{-2} .

To explore the kinetic behaviour of the oxides further, step polarization tests were performed. The lithium electrode was verified as practically unpolarizable in the current-density range explored. Moreover, in order to eliminate the influence of impurities on the first part of the discharge curves, the PbO and PbO_2 cells were discharged to a depth of 0.2 and 0.3 Faraday per mole, respectively. Step polarization measurements were then carried out, submitting the usual two-electrode cell to a sequence of galvanostatic pulses of short duration (about 30 s). As indicated in Fig. 6, PbO_2 behaves in a satisfactory way with voltages greater than 1 V up to current densities as high as 7 mA cm^{-2} .

Although cathodes where lithium insertion involves a displacement reaction resulting in extensive bond breakage and atom reorganization are generally not reversible near room temperature, explorative rechargeability tests were carried out. 10% graphite was added to the oxides in order to

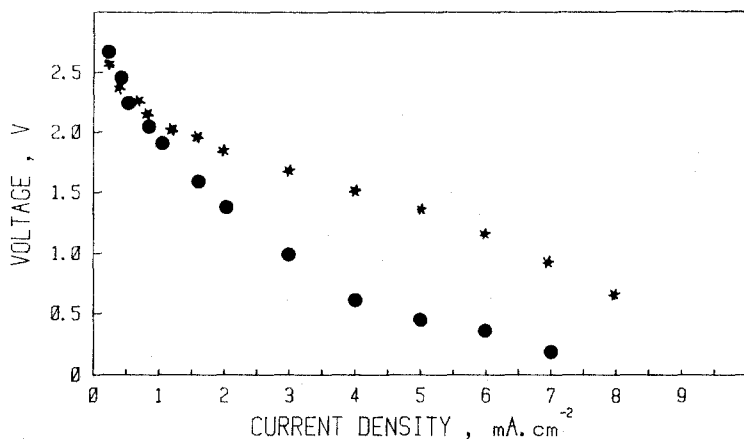


Fig. 6. Polarization values as a function of current density from step measurements in $1 \text{ M LiClO}_4\text{-PC}$ at room temperature: ●●●, PbO (Aldrich); *** , PbO_2 .