# Effect of silicate adsorption on the double layer capacitance and exchange current density of the Pb/PbSO$_4$ electrode reaction

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Galvanostatic transients in the linear polarization domain have been used to analyse the variation of double layer capacitance and exchange current densities of the Pb/PbSO$_4$ electrode reaction at various states-of-charge (SOC) values. From these data, the potential-dependence of double layer capacitance has been evaluated as a function of SOC. Interesting changes have been observed in the double–layer capacitance and exchange current densities as a result of immobilization of the electrolyte.

## 1. Introduction

The effect of adsorption on the electrode kinetics of specific reactions have received considerable attention in recent years because they can provide significant information in determining the fundamental behaviour of modified electrodes [1–4]. Determination of the adsorption-induced effects on both faradaic, as well as nonfaradaic processes occurring on the electrode–electrolyte interface, can be useful for designing electrocatalytic electrodes for several cases such as electrosynthesis [5], electroanalytical sensors [6], batteries and fuel cells [7], photoelectrolysis, corrosion inhibition [8] etc. For example, adsorption-induced irreversibility at low coverage [9], underpotential deposition [10–12] and adsorption dependent pseudocapacitance [13] are well known in several systems, and recent studies [14] indicate the remarkable advances in understanding the electronic and structural changes on well-defined single crystal surfaces as a result of adsorption induced reconstruction [13–15]. Some adsorbed species influence the electrode kinetics only through a change in the double layer structure, while others show specific chemical interactions with substrate, solvents and other adsorbates. Both inhibition and enhancement of electron transfer have been observed in a variety of reactions [16].

Since the adsorbed species can have a strong influence on the charge transfer kinetics of several reactions this can sometimes be used to improve the performance of existing electrochemical devices. For example, one class of rechargeable lead–acid batteries for maintenance-free applications employ thixotropic agents such as sodium silicate for immobilizing the electrolyte which produces adsorption induced benefits. Although these additives have been extensively used for about 35 years, their influence on the electrode kinetics of the Pb/PbSO$_4$ reaction has not been investigated so far except perhaps the effect on hydrogen evolution kinetics [17]. In addition, the utilization of both negative (Pb/PbSO$_4$) and positive (PbO$_2$/PbSO$_4$) electrodes have been found to be significantly affected by adsorbed silicate ions, as shown by the change in capacity values during discharge [18]. As a consequence, the gelled electrolyte obtained shows several superior design features compared to the conventional flooded-type such as minimum gas evolution due to electrolyte starving, increased corrosion resistance, increased safety against acid spills etc.

In this communication the effects of these immobilizing agents on the double layer capacitance and exchange current density of the Pb/PbSO$_4$ electrode are analysed by using potential–time transients. More specifically, the adsorption induced changes in exchange current density are evaluated at various SOC so that the insights obtained from such an analysis can be used to control the depth of discharge to attain higher cycle life of practical systems. Although these studies are based on macroscopic models, which do not directly give information about interfacial reactivity, the results are believed to be useful for designing immobilized systems for general applications.

## 2. Experimental details

Both the positive and negative electrodes used in this study were obtained in factory cured and formed conditions and the experimental details are described elsewhere [19, 20]. In brief, negative limited test cells with excess sulfuric acid (4.8 M) electrolyte were assembled with two positive counter electrodes (PbO$_2$) arranged on both sides of the working electrode (the apparent geometrical area of the electrode was 33 cm$^2$) along
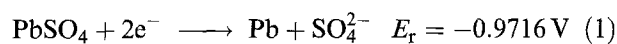
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with a Hg/Hg$_2$SO$_4$, H$_2$SO$_4$ reference electrode. All the electrodes used in the present study were made with same grid materials, namely Pb–Ca (0.08%)–Sn (0.5%), to preclude the possible effects of interaction by corrosion products from the grid. The Luggin capillary tip was aligned close to the working electrode to minimize the uncompensated resistance due to the solution. The potentials were measured accurate to $\pm 1$ mV by connecting a buffer amplifier with unity gain and substantially high input impedance ($10^{13} \Omega$) between the reference and working electrode. All experiments were conducted at a temperature of $25 \pm 1°$ C using millipore water and AnalaR grade reagents.

Initially, all the electrodes were soaked in a 4.8 M sulfuric acid for 10 h and then subjected to galvanostatic charging and discharging at $C/10$ and $C/8$ rates respectively. This was continued for five cycles to obtain stable capacity values and this constant value was used for all SOC calculations. All the cells were then given the same amount of overcharge (20%), kept at open circuit for 30 min and polarized with appropriate current densities such that the steady state could be obtained in few minutes within the linear polarization domain ($\eta \leqslant 10$ mV). On attaining the steady state, the current was interrupted and the potential transients were measured until the original equilibrium value was restored. The experiments were repeated using various current densities selected on the basis of causing negligible change in the SOC of the electrode (<0.01%). Similar transients were also obtained at other SOC values such as 0.8, 0.5, 0.2 and 0.05 by keeping the current density, as constant. These experiments were then repeated with separate electrodes at the same SOC values and current densities in an immobilized electrolyte. The latter was prepared by adding sodium silicate as a thixotropic agent, due to its well known property of existing, at low pH, as polysilicic acid [21].

## 3. Results and discussion

### 3.1. Analysis of potential–time transients

The major potential determining reactions occurring on a Pb/PbSO$_4$ electrode under open circuit conditions are

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-} \quad E_r = -0.9716 \, V \quad (1)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad E_r = -0.6186 \, V \quad (2)$$

and

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \quad E_r = +0.6116 \, V \quad (3)$$

Among these, the last reaction can be neglected as the dissolution of oxygen from atmosphere and its supply to the electrode surface by diffusion in a quiescent solution is very low. More significantly, a constant evolution of hydrogen observed experimentally on

open circuit initially saturates the solution with hydrogen at higher SOC values.

The Pb/PbSO$_4$ electrode under open circuit is in a steady state when current flows simultaneously due to the Pb/PbSO$_4$ and H$_2$/2H$^+$ electrode reactions. As a consequence, the observed potential is a corrosion potential (mixed potential) having contributions from anodic lead dissolution and cathodic hydrogen evolution reaction. The self discharge current or corrosion current is a manifestation of the equal and opposite currents due to Reactions 1 and 2. Under the assumptions of negligible mass transfer conditions the behaviour of the Pb/PbSO$_4$ electrode in the vicinity of the mixed potential region subject to anodic and cathodic polarization can be expressed as

$$I = -C_{dl}(dE/dt) + I_{0,Pb}[(\exp(-\alpha_{Pb}f\eta_{Pb})$$
$$- \exp(\beta_{Pb}f\eta_{Pb})] + I_{0,H}[\exp(-\alpha_H f\eta_H)$$
$$- \exp(\beta_H f\eta_H)] \quad (4)$$

where the first term corresponds to the nonfaradaic current with $C_{dl}$ as the double layer capacitance and the second and third terms correspond to faradaic currents associated with Reactions 1 and 2, respectively; $\eta_{Pb}$ and $\eta_H$ are the overpotentials for Reactions 1 and 2 defined as $E - E^r_{Pb}$ and $E - E^r_H$, respectively; $I_{0,Pb}$ and $I_{0,H}$ are the corresponding exchange current densities; $\alpha_{Pb}$, $\beta_{Pb}$, $\alpha_H$ and $\beta_H$ are the apparent charge transfer coefficients for the corresponding reactions and $f = nF/RT$, with $n$ as the number of electrons involved in the respective rate determining step. Although overpotentials and exchange current densities in Equation 4 can also be related to $E_{corr}$ and $I_{corr}$ values, respectively, this treatment is not general, as the corrosion rate is negligible at lower SOC values [19].

Consider a region close to equilibrium in the current–potential curve of this electrode; if the experimental conditions are judiciously selected so that the overpotential is very small ($\eta \ll 1/f$) the above equation can be written as [20, 22]

$$I = -C_{dl}\frac{dE}{dt} - f(E - E^r_{Pb})(\tau I_{0,Pb} + \alpha_H Q) + Q \quad (6)$$

where

$$Q = I_{0,H} \exp[-\alpha_H f(E^r_{Pb} - E^r_H)] \quad (7a)$$

and

$$\tau = (\alpha_{Pb} + \beta_{Pb}) \quad (7b)$$

The overpotential in Equation 6 includes the charge transfer component of the quasireversible Pb/PbSO$_4$ reaction and irreversible hydrogen evolution reaction (HER) in the Tafel domain. The ohmic component of the overpotential will also be a key parameter, controlling the kinetic behaviour especially at higher depth of discharge. This, however, may contain several parameters such as ohmic resistance of active material within the porous electrode, contributions from current collector, surface films, electrolyte and separator. A separation of these contributions is

highly desirable but does not seem to have been attempted, either theoretically or experimentally, for any general case as most of the practical systems include porous electrodes which are too complex for analysis [23]. Fortunately, the variation of ohmic resistance of active material with SOC is much larger compared to other contributions as this is even known to limit the capacity of porous battery electrodes due to pore-plugging [24]. Thus, an unambiguous determination of this ohmic drop is possible by including a SOC dependent resistance term in Equation 6. This term will be specially significant for maintenance-free operations with immobilized electrolyte as the ohmic drop due to the non-conducting materials (i.e. $PbSO_4$ along with the gel) is a key parameter to be minimized for high rate applications. Let $R_0$ denote this factor which will mainly depend only on the SOC of the electrode with other changes induced by immobilization. Hence the observed potential, $E$, in Equation 6 can be substituted by $(E + IR_0)$ with a correction for porous electrode resistance.

Thus an expression for the buildup and decay transients of $Pb/PbSO_4$ in sulfuric acid can be obtained as

$$I = -C_{dl}\frac{d(E + IR_0)}{dt}$$
$$-f(E - E_{Pb}^r + IR_0)(\tau I_{0,Pb} + \alpha_H Q) + Q \quad (8)$$

on recasting, with a constant $K = f(\tau I_{0,Pb} + \alpha_H Q)$,

$$I = -\frac{1}{1 + KR_0}\left[C_{dl}\frac{dE}{dt} + K(E - E_{Pb}^r) - Q\right] \quad (9)$$

This expression for potential–time transients is valid only if the diffusional contribution to overpotential is negligible. A high concentration of sulfuric acid (4.8 M), and invariance of potential time patterns with stirring, supports this assumption. More importantly, the current densities and time domain are selected to be extremely small so that time dependent diffusional contributions are rendered insignificant. Although the diffusional polarization is negligible due to these factors, when SOC is too high or too low, mass transfer becomes important and, hence, Equation 9 is invalid. In the intermediate range of SOC ($0 <$ SOC $< 1$) the above equation can be used to calculate both unknowns, $R_0$ and $K$ (which contains $I_{0,Pb}$). Since both are expected to vary with SOC (as SOC indicates the ratio of oxidant to reductant) at a particular SOC the buildup and decay (open circuit) transients can be expressed as

$$I = -\frac{1}{1 + KR_0}\left[C_{dl}\frac{dE}{dt} + K(E - E_{Pb}^r) - Q\right] \quad (10)$$

$$O = -\frac{1}{1 + KR_0}\left[C_{dl}\frac{dE'}{dt} + K(E' - E_{Pb}^r) - Q\right] \quad (11)$$

Subtracting Equation 11 from Equation 10 gives

$$I = -\frac{1}{1 + KR_0}\left[C_{dl}\left(\frac{dE}{dt} - \frac{dE'}{dt}\right) + K(E - E')\right] \quad (12)$$

If the potential is selected in such a way that the slopes of the decay and buildup transients can be compared at the same potential. $C_{dl}/(1 + KR_0)$ can be obtained. Thus,

$$\frac{C_{dl}}{1 + KR_0} = I\bigg/\left(\frac{dE'}{dt} - \frac{dE}{dt}\right) \quad (13)$$

From these $C_{dl}/(1 + KR_0)$ values the double layer capacitance can be easily obtained by plotting $dE/dt$ against $\eta$ according to Equation 8 which, on suitable rearrangement, gives

$$C_{dl}\frac{dE}{dt} = -I(1 + KR_0) - K(E - E_{Pb}^r) + Q \quad (14)$$

Thus by measuring the slopes of buildup $(dE'/dt)$ and decay $(dE''/dt)$ transient at a particular potential, $C_{dl}/(I + KR_0)$ values can be calculated at various SOC values. Furthermore, with these known $C_{dl}/(1 + KR_0)$ values and the slopes and intercepts of a plot of $(dE/dt)$ against $E - E_{Pb}^r$, $C_{dl}$ values can be calculated as a function of SOC. More specifically, the exchange current densities of the $Pb/PbSO_4$ reaction at various SOC can be calculated* by using the reported value of $I_{0,H}$ for HER on porous lead electrodes [25]. This evaluation of the fundamental kinetic parameters of the $Pb/PbSO_4$ reaction is important to the design of maintenance-free lead–acid batteries. The study of the variation of these parameters with immobilization of electrolyte also helps to improve their cycle life at high depths of discharge.

Although this analysis helps in calculating the kinetic parameters, namely $C_{dl}$ and $I_{0,Pb}$, the real utility is in calculating the potential dependence of the double layer capacitance at a given SOC, as this gives valuable information regarding the effects of adsorption. In addition, if adsorption of silicate causes any irreversibility, it will be reflected in the value of $I_{0,Pb}$, especially at lower SOC values.

### 3.2. Comparison of model with experimental data

Typical potential–time transients at various current densities (in the domain of $\eta$ less than 10 mV) for gelled and nongelled electrolytes at SOC = 0.5 are shown in Figs 1 and 2, respectively. The potential tends to reach the steady state value asymptotically with time and this time increases with an increase in the deviation from equilibrium. In addition, the buildup and decay patterns are much steeper for the gelled electrolyte. This may be attributed to the increased hindrance of mass transfer due to the presence of an interpenetrating net-work of polysilicic acid gel.

Comparison of the transients in Figs 1 and 2 illustrates that under cathodic polarization the overvoltage is higher when the electrodes are immersed in $H_2SO_4$ solution than in the case of $H_2SO_4$ gel.

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* These exchange current densities were calculated on the basis of apparent geometrical area ($33\,cm^{-2}$) as reliable information about the real surface roughness of the electrode could not be obtained.
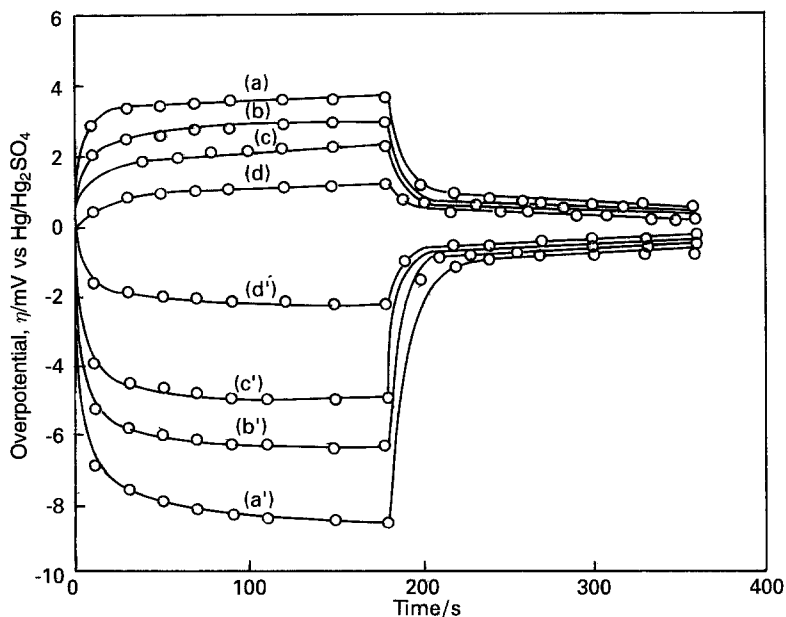
Fig. 1. Galvanostatic overpotential–time transients at various current densities for nongelled electrolyte at SOC = 0.5; (a), (b), (c) and (d) correspond to anodic transients and (a′), (b′), (c′) and (d′) correspond to cathodic transients at current densities of 60, 45, 30 and 15 μA cm$^{-2}$, respectively.

Under cathodic polarization, hydrogen evolution contributes more to the observed current (Equation 2) and the electrocatalytic effects of silicate adsorption for hydrogen evolution reaction [17] is mainly responsible. In contrast, under anodic polarization, the electrode in H$_2$SO$_4$ gel has higher overvoltage than that in H$_2$SO$_4$ solution as the predominant contribution under anodic polarization is due to Equation 1. This is consistent with the observation of lower exchange current densities for Reaction 1 in gelled electrolyte compared to that in H$_2$SO$_4$ solution.

Figures 3 and 4 show the variation of $I_{0,Pb}$ for the Pb/PbSO$_4$ system on changing the SOC of the electrode. These $I_{0,Pb}$ values were calculated on the basis of $C$ and $K$ values obtained from the slopes of Figs 1 and 2. These changes are consistent, indicating a change in the charge transfer kinetics of the electrode reaction with the ratio of the electroactive species. Probably the variation of $I_{0,Pb}$ with activities

of Pb(II) and Pb(0) with a correction for the change of activity of sulfuric acid may explain this variation. Irrespective of the source of the data (i.e. from cathodic or anodic transients) a large change is observed at SOC close to 1, corresponding to the onset of ideal polarizability under these conditions. Similar behaviour may be expected as SOC tend to zero, but the measurements were not conducted due to irreversible degradation. The difference in the magnitude for the cathodic and anodic cases can be ascribed to the contribution from the expected hydrogen evolution reaction.

The variation of double layer capacitance (calculated on the basis of apparent geometrical area) with SOC values for a prior anodic polarization case for the gelled and nongelled electrolyte is shown in Fig. 5. The variation from 0.2 to 0.8 is the representation of actual change, as higher SOC will have pseudocapacitance contribution from adsorbed hydrogen. Since the Pb/PbSO$_4$ electrode operates as
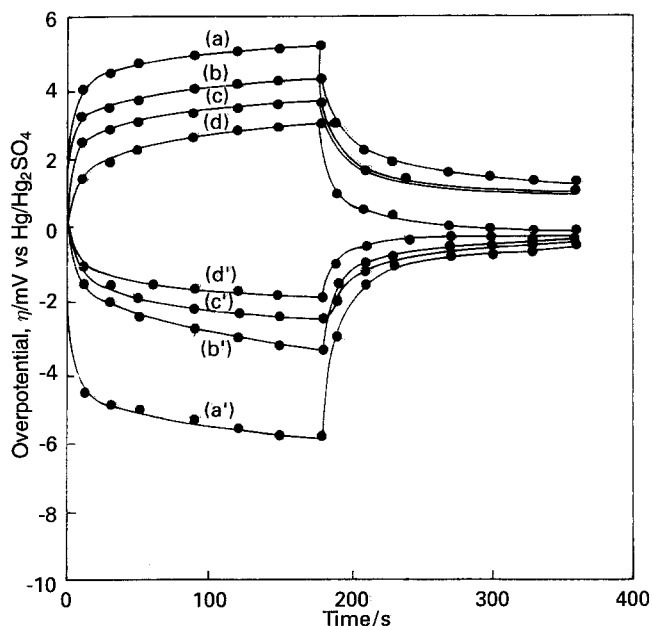


Fig. 2. Galvanostatic overpotential–time transients at various current densities for immobilized electrolyte at SOC = 0.5; (a), (b), (c) and (d) correspond to anodic transients and (a′), (b′), (c′) and (d′) correspond to cathodic transients at current densities of 60, 45, 30 and 15 μA cm$^{-2}$, respectively.
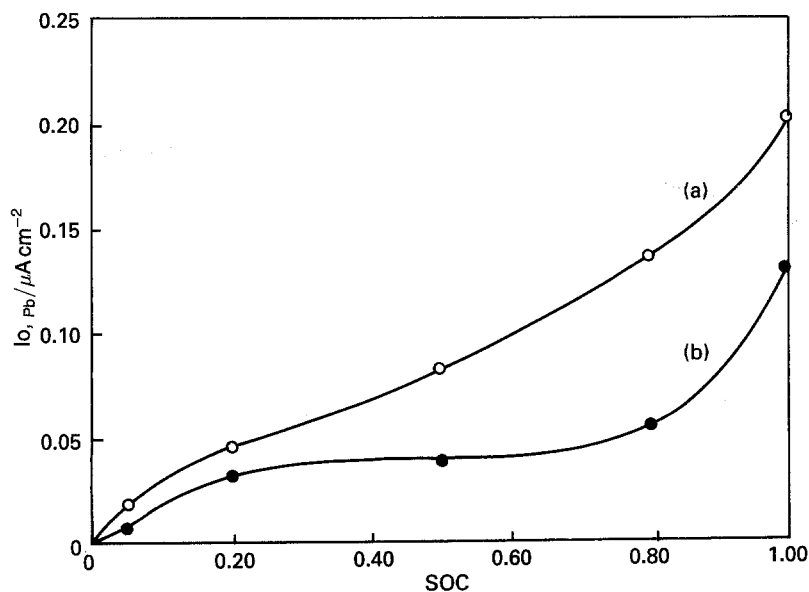
Fig. 3. Variation of $I_{0,Pb}$ with SOC obtained from the data from a prior cathodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.

an electrode of the second kind, through the dissolved Pb(II) species, the reversible potential is practically independent of SOC and the double layer is practically compact (Helmoltz type) due to the high ionic strength of the electrolyte [26]. Hence, the double layer capacitance should not vary appreciably in the range 0.2 to 0.8 SOC values as electrolyte depletion (including local alkalization in the pores) and adsorbed hydrogen can cause deviations at lower and higher SOC values.

The average value of $C_{dl}$ is less for the gelled case due to the adsorption of bulky silicate ions since the $C_{dl}$ is an indication of the area of the active material. Although this area is smaller for gelled electrolyte this trend is further enhanced in the case of SOC = 0.2, and the reduction in $C_{dl}$ is mainly due to the effects of adsorbed silicate ions, especially at low SOC values, where the silicate is masked by a large amount of $PbSO_4$ insulating layer. This decrease may be explained by the specific chemical interaction between $Pb^{2+}$ ions and silicate ions causing large leakage in capacitance.

Figure 6 shows the variation of double layer capacitance with SOC values for a prior cathodic polarization case. The large increase at unit SOC can be attributed to the contribution from adsorbed hydrogen which is negligible at very low SOC values. Similar trends with lower capacitance values are observed for the data from a prior anodic polarization case, as shown in Fig. 7. This is expected since the adsorption pseudocapacitance of hydrogen does not contribute in the anodic case. This change is in agreement with the observed cathodic shift in open circuit due to gelling (from −959 mV to −975 mV). Although the specific adsorption of silicate ions is expected to increase the capacitance, the capacitance seems to decrease as the potential becomes more cathodic. This trend can be attributed to the accumulation of insulating $PbSO_4$ on the pores of the electrode thus preventing the specific adsorption of silicate ions. This is increasingly clear for more anodic potentials.

The capacitance versus potential curve derived from potential–time transients during cathodic polarization at unit SOC is shown in Fig. 8. In this case the
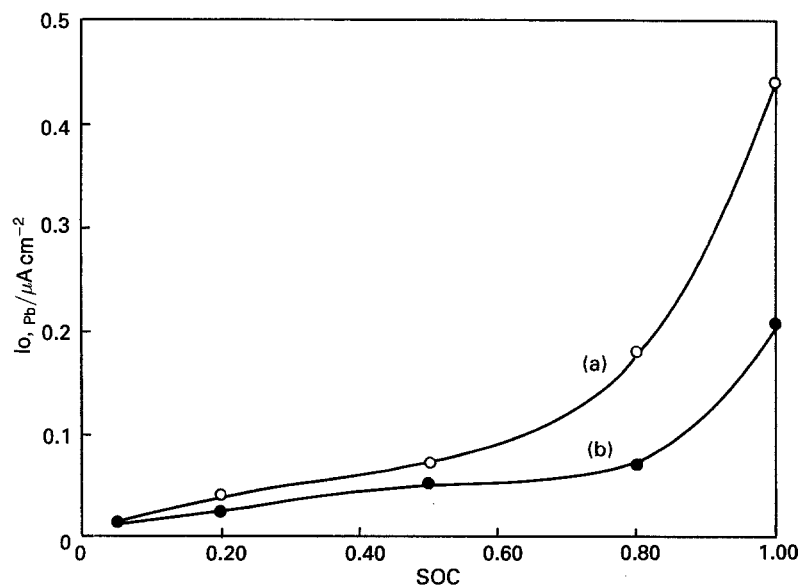


Fig. 4. Variation of $I_{0,Pb}$ with SOC obtained from the data from a prior anodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.
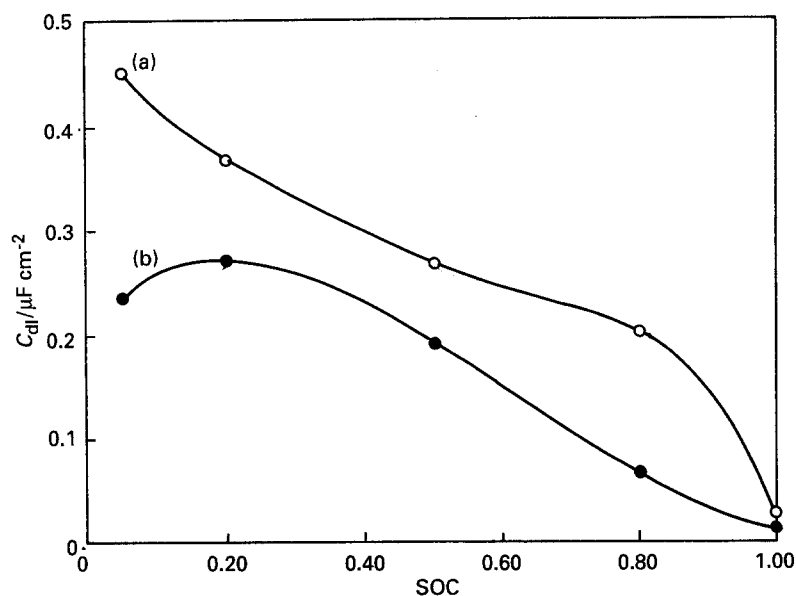
Fig. 5. Variation of $C_{dl}$ with SOC values for a prior anodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.
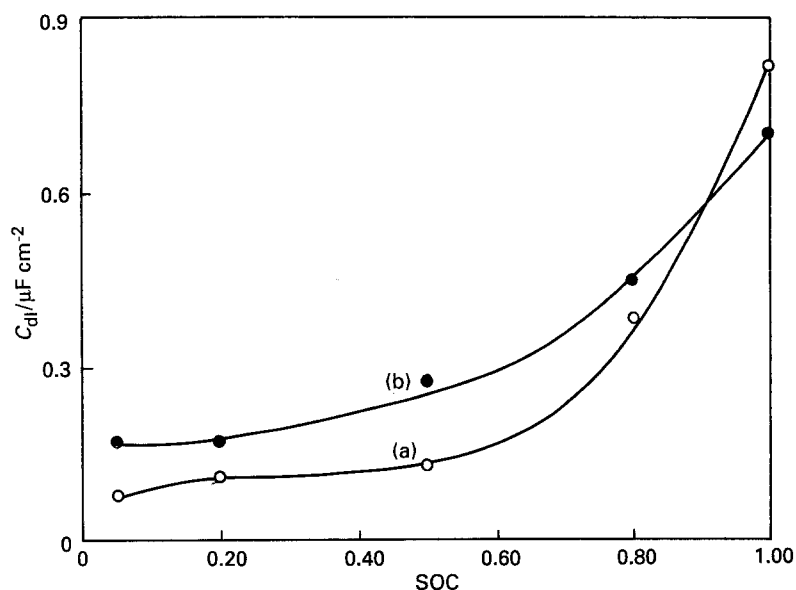


Fig. 6. Variation of $C_{dl}$ with SOC values for a prior cathodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.

contribution of hydrogen adsorption can also be significant, especially at high SOC values. Decrease in capacitance is also observed as a result of gelling. This effect can be attributed to the cooperative

adsorption of silicate ions and hydrogen, where the adsorbed silicate ions can electrocatalytically enhance the adsorption of hydrogen.
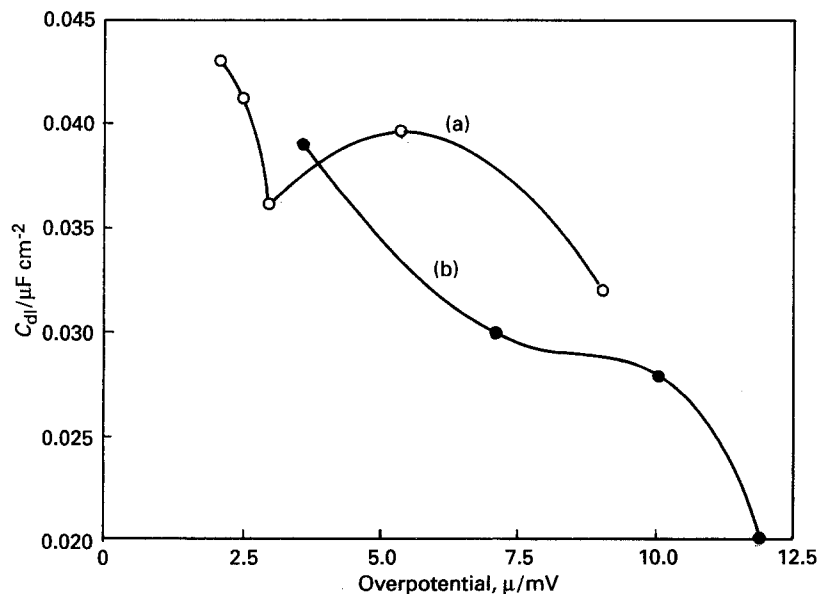
A comparison of Figs 7 and 8 shows that the



Fig. 7. Variation of $C_{dl}$ with overpotential for a prior anodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.
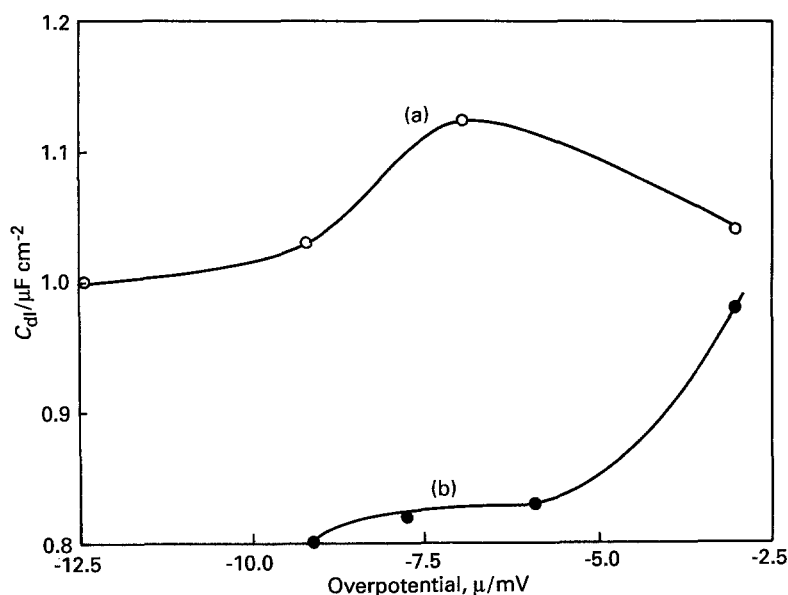
Fig. 8. Variation of $C_{dl}$ with overpotential values for a prior cathodic polarization case: (a) corresponds to nongelled electrolyte and (b) corresponds to immobilized electrolyte.

capacitance values are larger when obtained from the data for a prior cathodic polarization. During anodic polarization, the variation of coverage with potential (due to the accumulation of insulating $PbSO_4$ in the pores) is mainly responsible for the capacitance changes.

### 3.3. Limitations of the model

One of the major assumptions involved in deriving Equation 14, i.e. the quasireversibility of the $PbSO_4$ system, may not be universally valid, especially because near the open circuit potential both lead dissolution and cathodic hydrogen evolution reaction occur at equal rates, due to self discharge (corrosion) process. For cathodic polarization at high SOC values this quasireversibility may not be valid as hydrogen evolution is the only possible reaction and current passed is completely utilized for Reaction 2. Similarly, at very low SOC values all the faradaic currents are completely used for Reaction 1, and departure from quasireversibility may be expected. As a consequence the model is not valid at both high (close to unity) and low (close to zero) SOC values.

Another major disadvantage of the above model arises from neglect of adsorption induced pseudo-capacitance. This is more important for cathodic polarization as adsorbed hydrogen can contribute to all parameters estimated using the above model. More specifically, the coverage induced variations of exchange current density and $C_{dl}$ contains large errors. Lastly, at high SOC values $I_{0,Pb}$, estimated using this model, reflects the corrosion currents for the $Pb/PbSO_4$ system rather than the true $I_{0,Pb}$. In contrast, at lower SOC values, the estimated exchange current has a more significant contribution from the $Pb/PbSO_4$ system, particularly for cathodic polarization, as hydrogen evolution cannot occur since there is very little, if any, free lead present.

### 4. Conclusion

The behaviour of the $Pb/PbSO_4$ electrode in maintenance-free lead–acid batteries has been successfully investigated. A quantitative analysis of the potential–time transients explains the observed effect of adsorbed silicate ions on the exchange current densities and double layer capacitance of the system. These results are useful in understanding the potential dependence of the double layer capacitance at particular SOC values.

### Acknowledgements

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