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Chemical Sensing of Amine Antioxidants in Turbine Lubricants

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A chemically modified microelectrode has been developed for the determination of amine antioxidants in turbine lubricants. The electrochemical probe is coated with a thin film of conducting poly(ethylene oxide), which, when placed into a lubricant environment, results in the extraction of the electroactive species into the polymer. Cyclic voltammetric experiments have been performed and an ability to measure the phenyl-α-napthylamine additive quantitatively has been demonstrated.

Keywords: *Chemical sensor; cyclic voltammetry; amine antioxidant; poly(ethylene oxide); lubricant*

The analysis of lubricating oils during or after use is an established approach for determining the extent to which they might have deteriorated or been contaminated during operation in an engine. This is commonly carried out by removing samples for analysis. There are many tests that are routinely used, a combination of which is generally suitable for determining the condition of the lubricant, or diagnosing problems with the engine. Analytical techniques are typically employed to determine changes in physical properties such as viscosity, acidic content, colour, odour, water content and flash point.[1] However, from these measurements, it is not possible to determine the remaining useful lifetime of a lubricant.[2] It has been demonstrated that lubricants rapidly degrade as the concentrations of antioxidant additives decrease,[3] indicating the importance of being able to monitor additive concentration in oils as operating time progresses. Indeed, the concentration of antioxidant is used as an important indicator of the remaining useful lifetime, and a number of methods[4,5] are presently used in its determination, including electrochemical techniques.[6,7] However, with these methods the measurement cannot be made *in situ* without sample pre-treatment. In this study, the possibility of introducing a single technique that could be used *in situ*, or at least could be applied easily without additional sample preparation, to used oil samples has been explored. Such a method could be very attractive in providing a rapid on-the-spot analysis of the lubricant, which has previously not been possible.

The proposed approach uses an electrochemical probe for direct chemical sensing of amine antioxidants in turbine lubricants. The resistance of a typical turbine lubricant is so high that standard electrochemical experiments, which require a conductive medium, are impossible. Therefore, a micro-electrode has been chemically modified[8] so that the electrochemistry of the amine antioxidant can be monitored.

Experimental

Probe Construction

A schematic representation of the electrochemical probe that was developed for this work is shown in Fig. 1. The three-electrode arrangement was constructed by feeding three metal wires through the end of a soda-glass tube before heat-sealing. The extreme tips of the wires were then exposed by careful polishing, using emery paper followed by a succession of 1, 0.3 and 0.04 μm alumina polishes. The wires were positioned inside glass sleeves to ensure they were electrically insulated from each other and then connected to metal terminal caps. The Ag wire acted as a pseudo-reference, the Pt wire as a counter electrode and the Pt microdisc as a working electrode. The arrangement was then coated with a polymer film cast from a solution of poly(ethylene oxide) [PEO; Aldrich, average relative molecular mass (M_r), 600 000] and LiClO$_4$ in acetonitrile–methanol (9 + 1, by volume). These chemisorbed

films are typically about 10 μm thick and have the composition PEO$_{16}$LiClO$_4$.
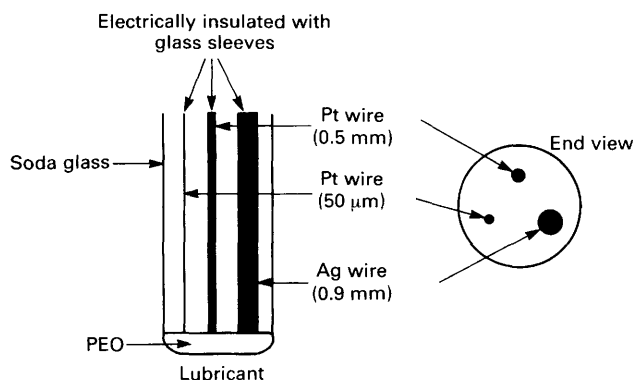
Apparatus

An EG & G Model 173 potentiostat and Model 175 programmer were used for the electrochemical experiments and current–potential data were recorded on a Gould 1604/104 storage oscilloscope. The sample temperature was kept constant to within 0.5 °C using a thermostatically controlled water-bath.

Method

Typically, 25 μl of the polymer–salt solution was dispensed onto the end of the polished electrode, and evaporation and curing of the film were allowed to take place for 10 min at 50 °C. The electrochemical probe was then placed in the oil sample (1–2 ml) at an elevated temperature (about 60 °C). After a set time (10 min), a cyclic voltammogram (CV) was recorded at a sweep rate of 200 mV s^{-1}.
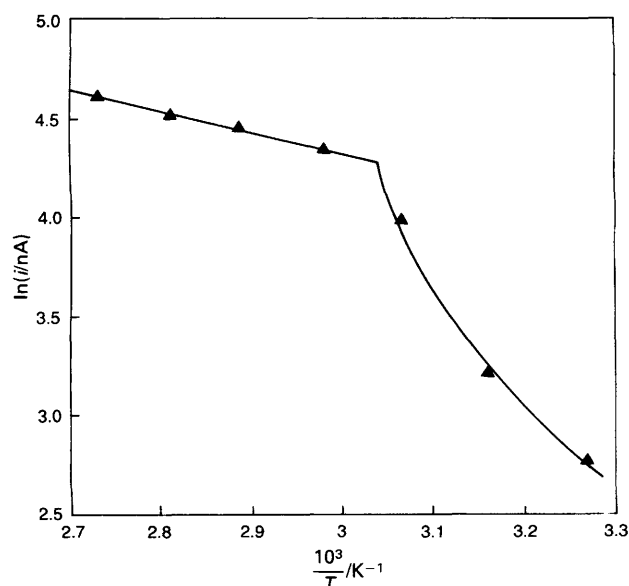
Results and Discussion

Unused base oil with no additive species present shows a featureless CV between the cathodic and anodic limiting currents [see Fig. 2(*a*)]. These limiting currents register the onset of the decomposition of the polymer matrix. Comparison of this with the CV of the fully formulated oil [Fig. 2(*b*)] reveals three distinct features attributable to the presence of additives in the formulation. Samples of the individual additives dissolved in the base oil, giving concentrations equivalent to those in the formulated oil, were prepared. From the CVs, it was apparent that the peaks marked A and B in Fig. 2(*b*) can be assigned to the amine antioxidant,

Electrically insulated with glass sleeves

Soda glass

Pt wire (0.5 mm)
Pt wire (50 μm)
Ag wire (0.9 mm)

End view

PEO

Lubricant

Fig. 1 Schematic representation of the three-electrode electrochemical probe with an ionically conducting PEO film
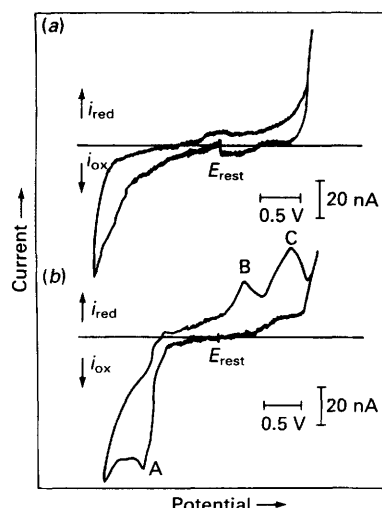
Fig. 2 Cyclic voltammograms of (*a*) a base oil with no additives and (*b*) a fully formulated turbine lubricant. Peaks A and B can be assigned to PAN and peak C to a rust inhibitor also present in the formulated oil
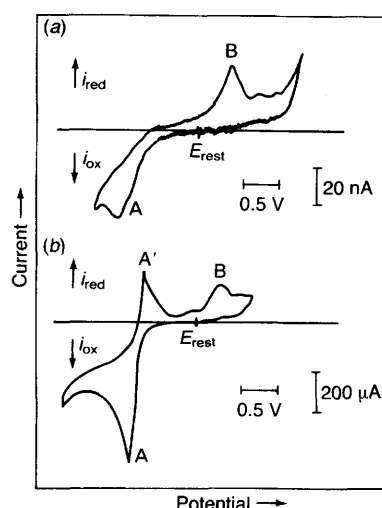

Fig. 4 Cyclic voltammograms of (*a*) PAN in base oil (polymer-coated electrode) and (*b*) PAN in acetonitrile–0.1 mol dm^{-3} Bu$_4$NBF$_4$ (Pt-wire electrode). For details of peaks labelled A, A′ and B see text

Fig. 3 Plot of voltammetric peak current [peak A (see text for details)] as a function of 1/T for PAN in a turbine lubricant

phenyl-α-naphthylamine (PAN), and peak C to a rust inhibitor also present in the formulated oil.

The PEO film is polar in nature and has an affinity towards polar molecules in the oil, such as the amine antioxidant. Although high M_r polymers, such as PEO, exhibit mechanical properties that are similar to those of a true solid, at the atomic level, local relaxation processes still provide liquid-like degrees of freedom.[9] These give rise to ionic conductivity, with ion transport considered to take place by a combination of motion linked to both movement of the polymer segments and ion transition between suitable coordination sites. At elevated temperatures, the ionic conductivity is such that the electrochemistry of the preconcentrated additive species can be successfully observed at the working microelectrode. For this type of electrochemical experiment PEO is ideal because it is relatively resistant to oxidizing and reducing conditions, and gives a reasonably large electrochemical window in which to observe additive species.

A sample of the formulated oil was taken, and the peak current for the oxidation of the PAN additive [Fig. 2(*b*), peak

A] recorded as a function of the increasing temperature. The relationship between the two is represented in an Arrhenius-type plot (Fig. 3). It can be seen that the peak current increases in a similar manner to the way that ionic conductivity has been observed to increase with temperature.[10] This reflects the mobility of the additive species in the PEO matrix and can be explained in terms of the 'free-volume model'.[11] As the temperature is increased, the expansivity of the polymer produces local empty spaces (free volume) into which ionic carriers or polymer segments can move. The curve in Fig.3 shows an abrupt change in slope at about 56 °C, which can be traced to a change in phase of the polymer. At room temperature, PEO has a variety of morphologies and consists of both crystalline and amorphous phases. This multi-phase behaviour strongly influences the transport of species. As the temperature is raised above the glass transition temperature (T_g), a rapid increase in the observed current is seen and the PEO becomes macroscopically rubbery, rather than glassy. This means that the local environment around any given polymer chain becomes liquid-like. Above the T_g, the increase in current with a rise in temperature is much less rapid. Therefore, in terms of the operating conditions for the probe, it would seem advantageous to work at temperatures above the T_g, where large currents are observed and the morphology of the PEO is not variable, thus improving the reproducibility of the data obtained.

The electrochemistry of PAN in acetonitrile was also studied at a Pt wire electrode, using Bu$_4$NBF$_4$ as a supporting electrolyte and Ag–AgNO$_3$ (0.1 mol dm^{-3}) as the reference. The CV obtained at a sweep rate of 200 mV s^{-1} is given in Fig. 4,, along with the CV of PAN in base oil recorded using the polymer-coated electrode. The peak marked A′ in the CV from the acetonitrile solvent shows that the oxidation peak, A, is part of an electrochemical couple. Additional CVs demonstrated that the peak current of A was proportional to the square root of the sweep rate (for v <500 V s^{-1}), and that the peak potential was independent of sweep rate. It was noted that peak B was only observed if the initial sweep direction of the CV was in the anodic direction. This would indicate the existence of the following reaction scheme:
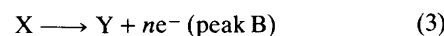
$$R + ne^- \rightleftharpoons O \text{ (peaks A and A′)} \qquad (1)$$

$$O \xrightarrow{k} X \qquad (2)$$

$$X \longrightarrow Y + ne^- \text{ (peak B)} \qquad (3)$$

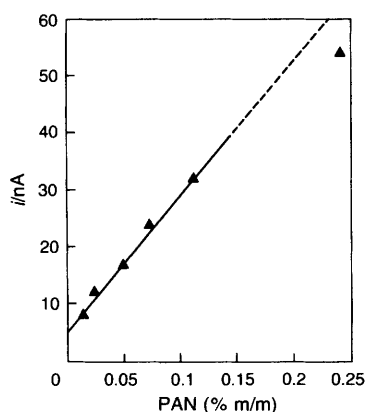**Fig. 5** Reaction of PAN at a Pt electrode to form a cation radical

Fig. 6 Relation between voltammetric peak current [peak A (see text for details)] and concentration of PAN

The oxidized species (O) is partially consumed in a chemical reaction that produces another species (X), the reduction of which gives rise to peak B. The values of the reaction rate (k) and sweep rate (v) are such that the A–A' couple is not completely reversible. The actual oxidation involved is likely to be as shown in Fig. 5.[12] Although some stability is conferred to the cation radical by the phenyl and naphthyl systems, this species is sufficiently unstable to be consumed in the subsequent chemical reaction. Peak B, compared with peak A, is much larger under the base oil–polymer conditions than it is under the acetonitrile–Pt wire electrode conditions. In addition, peak A' does not feature in the solid electrolyte, indicating that the diffusion coefficients and reaction rate constants in the polymer matrix and solvent are different.

A study was carried out to establish if the magnitude of the oxidation current of peak A could be related to the concentration of PAN in a lubricant package. All of the CVs were recorded after a set time in order to allow the polymer–lubricant interface to equilibrate (eqn. 4)

$$[PAN]_{oil} \rightleftharpoons [PAN]_{PEO-LiClO_4} \qquad (4)$$

The magnitude of the current is dependent on the ionic conductivity and the thickness of the polymer film, in addition to the diffusion coefficients of the electroactive species dissolved in the polymer.[13] Constant temperature was therefore required to achieve reproducible data. A series of solutions with varying concentrations of PAN in base oil were prepared. The electrode was polished and a fresh polymer-film coated onto the surface for the analysis of each sample. The response of each new polymer-coated electrode, in a sample of the fully formualted oil, was used as a reference for the signal obtained for the antioxidant. The current observed for peak A is plotted against % m/m PAN in Fig. 6. A reasonably linear response was obtained over the range 0–0.15% m/m PAN, a span that encompasses the concentration of the antioxidant in the fully formulated lubricant. At higher concentrations (0.2% m/m PAN), non-linearity ocurred probably because of an uncompensated iR (current × resistance) drop or possibly even from saturation of the polymer film.

The electrochemical probe has been used to monitor the depletion of the PAN additive in an oil during a turbine oil stability test[14] by taking samples from the test rig at regular intervals. The error associated with this electrochemical analysis was of the order of 5%, which permitted the trend of additive consumption to be satisfactorily followed over a period of time.

Towards the end of the lifetime of a turbine oil, neutral and acidic degradation products are known to build up. Samples of used oil, which were known to have these products present, were taken and their CVs recorded using the polymer-coated electrode. It was shown that these degradation products do not produce interferences at the potential for which the electroactivity of the antioxidant is observed.

Conclusions

An approach for establishing an ionically conducting medium into which additive species can be extracted from a poorly conducting oil environment, for quantitative analysis, has been demonstrated for the amine antioxidant PAN in a turbine lubricant. The experiment can be simplified from one of cyclic voltammetry to a simple potential step at which the additive is known to oxidize, and by monitoring the steady-state current after a set time. The electronics required for such an arrangment could conceivably be miniaturized into a simple hand-held device with some additional facility to enable constant temperature to be maintained during the analysis of oil samples. Of greater attraction is the ability to place a sensor directly into a working environment to give continuous on-line monitoring. Initial work on PEO indicates that it is physically robust and is capable of retaining reasonable levels of ionic conductivity over periods of several days. The ability to perform this type of sensing is attractive, although technically demanding, with the reliability and durability of the probe becoming crucial factors, along with the ability to calibrate and reference the recorded signals. The ability to monitor the oil condition *in situ* is desirable in terms of providing more accurate information on drain-time requirements and to provide a forewarning of oil degradation brought about by unusual operating conditions. The conducting polymer-coated electrode would appear to hold some promise in achieving these goals, with respect to monitoring amine antioxidants in turbine lubricants.

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