Cyclic voltammetric study of quinone–hydroquinone organic system in aqueous magnesium perchlorate electrolyte

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Abstract

This paper reports cyclic voltammetric investigations of the quinone–hydroquinone redox system in aqueous magnesium perchlorate medium containing different concentrations of p-benzoquinone. The studies have been performed on a glassy-carbon electrode and have furnished information on (i) the separation in potential (ΔE_p) between the anodic and cathodic peaks, (ii) the anodic and cathodic peak currents, and (iii) the ratio of the anodic and cathodic charges (Q_a/Q_c) and the relationship of all three parameters with sweep rate. The interrelationship of ΔE_p or Q_a/Q_c with scan rate gives information that is almost in agreement from the view point of battery applications. The system exhibits best performance at an 8 mM concentration of p-benzoquinone.

Introduction

Among the various known organic depolarizers, investigations on the quinone–hydroquinone redox system have evoked considerable attention during past decades [1–3]. An extensive survey of the subject [4, 5] reveals that information is available on more than 200 organic compounds. The best organic depolarizers can be classified into four types: (i) nitro compounds (RNO_2); (ii) positive halogen compounds (ROX and RNX); (iii) halogen addition compounds (R_3NX_2), and (iv) peroxides (ROOR). Among these compounds, nitro compounds (e.g., m-dinitrobenzene) possess, theoretically, 1.91 Ah g^{-1} output capacity. This is primarily due to the transfer of many electrons during the reduction process [6, 7]. These compounds do not, however, exhibit good reversible behaviour, nor has it been possible to realize in practice the capacity that is expected from them.

As it is well known, oxidation and reduction reactions in organic chemistry are irreversible in nature. An exception to this is the group of compounds involving quinoid–benzonoid reaction equilibria. The quinone–hydroquinone redox reaction has

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been considered [8] to be one of the best reversible systems. The potential of the system was evaluated by Hovorka and Dearing [9] to be:

$$\text{(p-benzoquinone)} + 2H^+ + 2e^- \rightleftharpoons \text{(hydroquinone)} \qquad E^0 = +0.699 \text{ V}$$
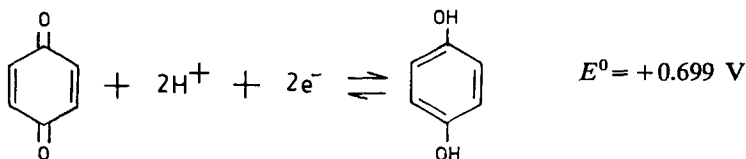
Earlier work [10, 11] on the quinone–hydroquinone system indicates that quinone, or its substituted compounds, is considered as a promising candidate for the use in primary as well as secondary batteries. Capson and Parsons [12] selected N,N'-dimethylformamide (DMF) as an ideal test solvent for the reduction of p-benzoquinone using six different working electrodes, viz., Pt, Pd, Ir, Rh, Au and Hg. Although many developments in the past have stimulated detailed electrochemical studies on metallic and nonmetallic electrode materials other than conventional mercury, the number of solid-electrode materials available for electroanalytical applications is still very limited. This is especially true in the case of voltammetric studies, which are of interest to this work. Of the few electrodes described by Adams [13], only Pt, Au and a few types of carbon electrodes have found use in voltammetric applications. Since, the former type of metallic electrodes is sensitive to oxidation/reduction reactions, care must be exercised in the interpretation of data involving adsorbed species. Also, these low hydrogen-overvoltage materials may not be of great use in the cathodic region. In order to circumvent these problems, and to have a reproducible surface for a good redox process such as quinone–hydroquinone, we have employed a glassy-carbon electrode. This is the latest addition to the list of carbon electrodes for electroanalytical applications [14, 15]. In view of these facts, the electrochemical redox behaviour of p-benzoquinone on a glassy-carbon electrode (GC) surface has been investigated in a magnesium perchlorate supporting electrolyte. It should be noted that this electrolyte is important in battery-related devices [16–19].

Experimental

Cyclic voltammetric measurements were performed at 25 ± 0.5 °C by means of a potentiostat (Tacussel PRT 20-2X) coupled to a voltage–scan generator (Wenking VSC-72) and an x–y recorder (Rikadenki). Tafel studies were carried out using a BAS 100A electrochemical analyser. All reagents were of analytical grade and the solutions were prepared in double-distilled water. A stock solution of 0.3 M magnesium perchlorate was prepared by dissolving the required quantity of $Mg(ClO_4)_2 \cdot 6H_2O$ in water. Since p-benzoquinone is insoluble in water, its solution of 0.1 M concentration was made in 100% DMF immediately prior to each experiment. The latter were carried out in a conventional three-electrode cell assembly. Glassy carbon (A grade; exposed area: 0.0707 cm^2), fitted tightly into a Teflon holder, was used as the working electrode. The electrode surface was mechanically pretreated and polished with 2/0, 3/0, 4/0 and 5/0 emery papers, degreased with acetone, and finally washed with water before use. A platinum foil of large area was used as the auxiliary electrode. All the potentials are reported with respect to a Ag/AgCl (1 M HCl) reference electrode. Before the start of each series of experiments, an inert gas was passed through the cell for 30 min. A period of 15 min was allowed for the system to reach a steady-state, open-

circuit potential. A triangular potential pulse was applied between the potential range 300 to −500 mV and was scanned at different sweep rates, viz., 0.02, 0.04, 0.1, 0.2, 0.3 and 0.4 V s⁻¹. A conventional method [20] was used to measure the peak currents.

Results and discussion

Prior to the addition of p-benzoquinone to the electrolytic cell, cyclic voltammograms were recorded by a blank electrolyte of 0.3 M Mg(ClO₄)₂, see Fig. 1. No peaks were observed and this suggests that the magnesium perchlorate is neither oxidized nor reduced in the potential range employed for this study. On addition of different concentrations of p-benzoquinone (2–10 mM), however, well-defined cathodic and anodic peaks were produced (Figs. 2 and 3). These indicate the existence of a p-benzoquinone–hydroquinone redox couple.

Plots of the cathodic peak currents against the square root of the sweep rate exhibit a linear relationship, as indicated in Fig. 4. In the case of low concentrations (i.e., up to 4 mM), the straight lines, when extended, pass through the origin and, hence, electron transfer at the metal/Helmholtz interface is subject to a simple diffusion-controlled process. Beyond a 4 mM concentration of p-benzoquinone, however, the linear plots do not pass through the origin. This suggests the occurrence of a process comprising both diffusion- and kinetically-controlled reactions. Similarly, the anodic peak currents vary linearly with the square root of the scan rate. As the difference in the anodic and the cathodic peak potentials is considered to be an indication of the degree of reversibility, the variation of ΔE_p with respect to concentration and sweep rate is presented in Table 1. The greater the value of ΔE_p, the greater will be the irreversibility of the redox process. In terms of batteries, the variation of electrode potential between 300 and −500 mV at different sweep rates corresponds to a similar
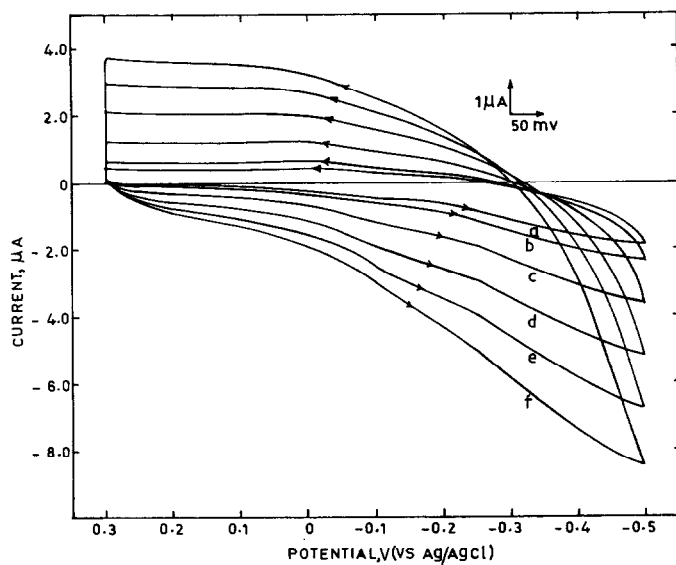

Fig. 1. Cyclic voltammograms for 0.3 M magnesium perchlorate on a glassy-carbon electrode at different scan rates (mV s⁻¹): (a) 20; (b) 40; (c) 100; (d) 200; (e) 300, and (f) 400.
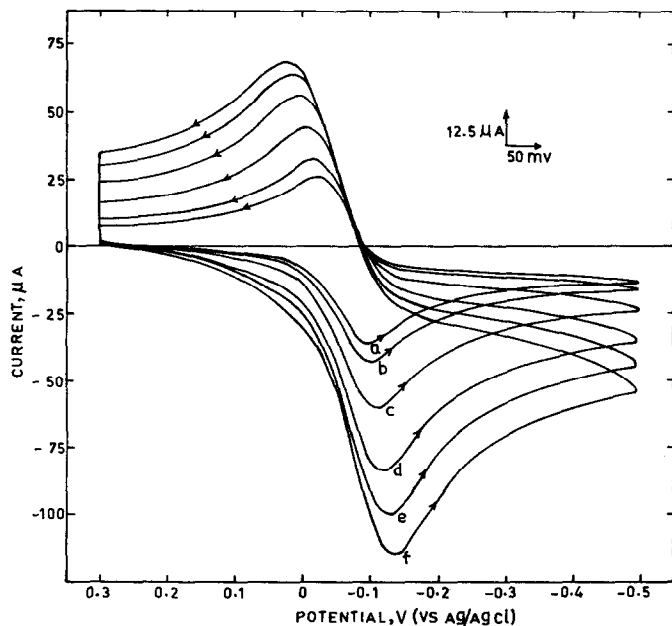
Fig. 2. Typical cyclic voltammograms for p-benzoquinone (8 mM) in 0.3 M magnesium perchlorate on glassy-carbon electrode at different scan rates (mV s^{-1}): (a) 20; (b) 40; (c) 100; (d) 200; (e) 300, and (f) 400.

situation of cycling an electrode at different rates. These data are shown in Fig. 5. From the view point of a battery application, the extrapolation of the peak separation to zero sweep rate could help to evaluate the electrode behaviour near the reversible potential. The observation of a minimum ΔE_p at zero sweep rate corresponds to the maximum reversibility of the electrode. Our data indicate that the $(\Delta E_p)_v = 0$ value is minimum (i.e., 0.075 V) at an 8 mM concentration of p-benzoquinone.

Quantitatively, the greater the peak current, the greater will be the charge acceptance or the ease of charging of the quinone electrode when employed in a battery. For this purpose, an integration of both the anodic and cathodic areas in the voltammograms has been made in order to evaluate a parameter called 'charge' which is presented in Table 2. The ratio of the anodic and cathodic charges, when plotted against sweep rate (Fig. 6), supplements the information with respect to the best reversible system. That is, Q_a/Q_c is considered to be unity for an ideal reversible system. Extrapolation of Q_a/Q_c to the zero sweep rate, i.e., $(Q_a/Q_c)_v = 0$, is a measure of the reversibility of the electrode as well as its charge/discharge efficiency. As is evident from Fig. 6, the ratio at zero sweep rate is almost equal in case of 8 and 10 mM concentrations, i.e., 0.88 and 0.92, respectively. The Q_a/Q_c rate deviates significantly from unity at higher sweep rates. This indicates the low charge/discharge efficiency of the quinone electrode at higher rates of cycling. It may be inferred from these results that the glassy-carbon/quinone interface exhibits best reversibility and charge/discharge efficiency at an 8 mM concentration of p-benzoquinone (the relationships of ΔE_p or Q_a/Q_c with sweep rate give information that are almost in agreement).

Tafel studies have been carried out by selecting the applied potential range from the rising portions of cathodic and anodic peaks at all concentrations of p-benzoquinone
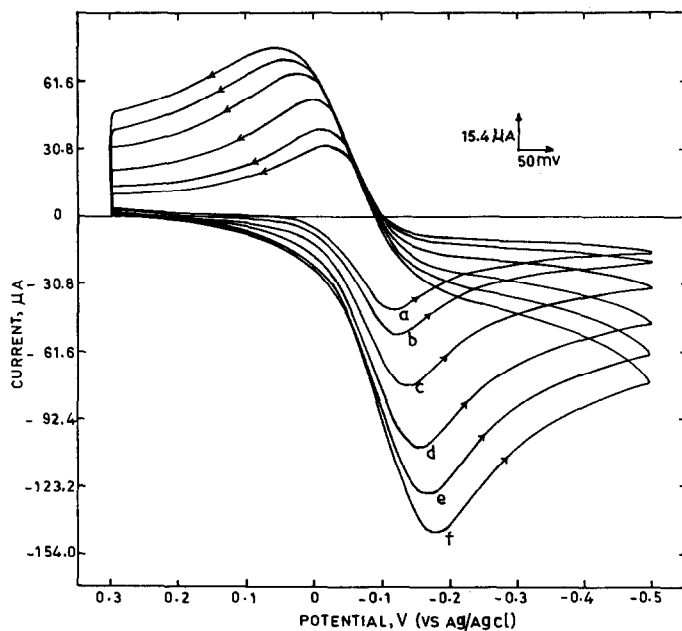
Fig. 3. Typical cyclic voltammograms of p-benzoquinone (10 mM) in 0.3 M magnesium perchlorate on glassy-carbon electrode at different scan rates (mV s^{-1}): (a) 20;·(b) 40; (c) 100; (d) 200; (e) 300, and (f) 400.
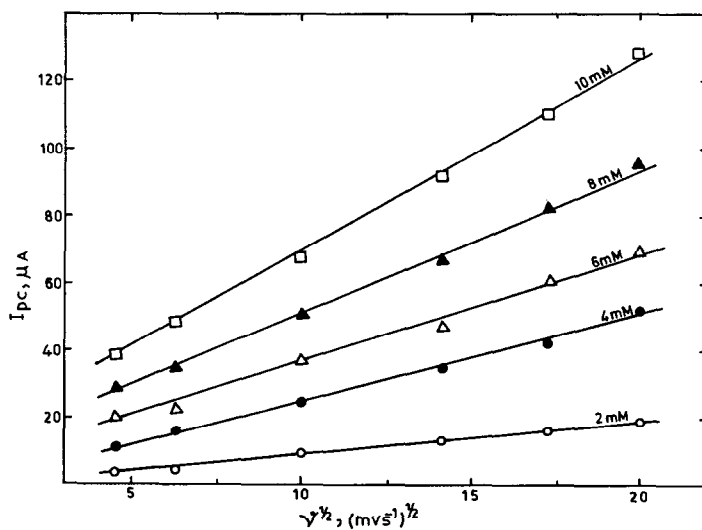

Fig. 4. i_{pc} vs. square root of scan rate for different concentrations of p-benzoquinone.

at typical sweep rates of 1 and 20 mV s^{-1} (Figs. 7 and 8). Extrapolation of the linear portions of the respective plots to the y-axis provides a measurement of the exchange current density (i_0). The resulting values are given in Table 3. It is evident that,

TABLE 1

Data on peak potential separation, ΔE_p (mV), for different concentrations of p-benzoquinone at different sweep rates

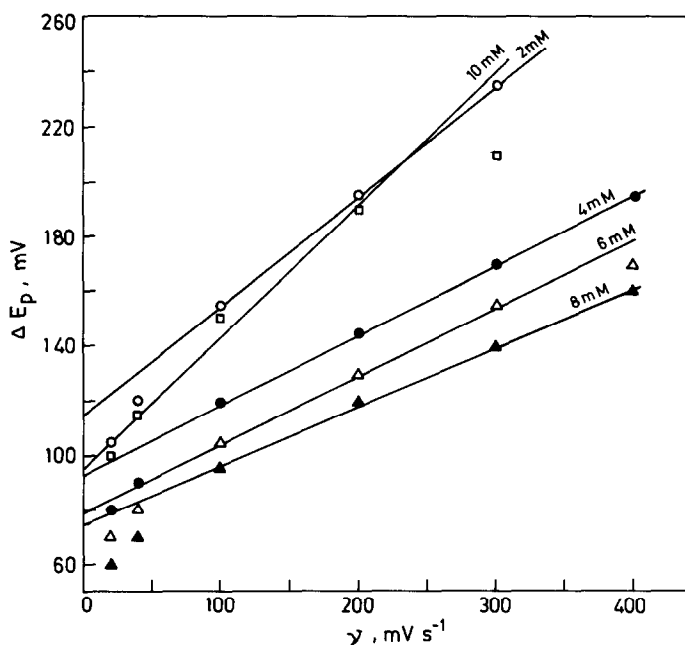| p-Benzoquinone concentration (mM)	Sweep rate (mV s^{-1})					
	20	40	100	200	300	400
2	105	120	155	195	235	255
4	80	90	120	145	170	195
6	70	80	105	130	155	170
8	60	70	95	120	140	160
10	100	115	150	190	210	225

Fig. 5. ΔE_p vs. scan rate for different concentrations of p-benzoquinone.

irrespective of the sweep rate selected, i_0 is more or less maximum at 8 mM concentration. Again, this is in agreement with results given above.

Conclusions

The ratio of anodic and cathodic charge has been found to be almost unity in the low range of sweep rates. This indicates a good charge/discharge behaviour at low rates of cycling of the cell based on the quinone electrode. Amongst the different p-benzoquinone concentrations studied, it is found that the redox behaviour is optimum at 8 mM in terms of both the electrode reversibility and the anodic-to-cathodic charge

TABLE 2

Data on charge, $Q(\text{mC cm}^{-2})$, obtained from the cyclic voltammograms

| p-Benzoquinone concentration (mM)	Anodic, Q_a Sweep rate (mV s^{-1})						Cathodic, Q_c Sweep rate (mV s^{-1})					
	20	40	100	200	300	400	20	40	100	200	300	400
2	0.035	0.026	0.012	0.007	0.003	0.004	0.054	0.036	0.021	0.014	0.009	0.011
4	0.099	0.064	0.035	0.022	0.010	0.013	0.119	0.079	0.043	0.034	0.017	0.024
6	0.168	0.104	0.059	0.036	0.018	0.024	0.166	0.113	0.075	0.049	0.026	0.034
8	0.266	0.153	0.086	0.056	0.027	0.036	0.266	0.219	0.102	0.069	0.035	0.047
10	0.347	0.202	0.108	0.069	0.033	0.042	0.350	0.214	0.125	0.084	0.045	0.063
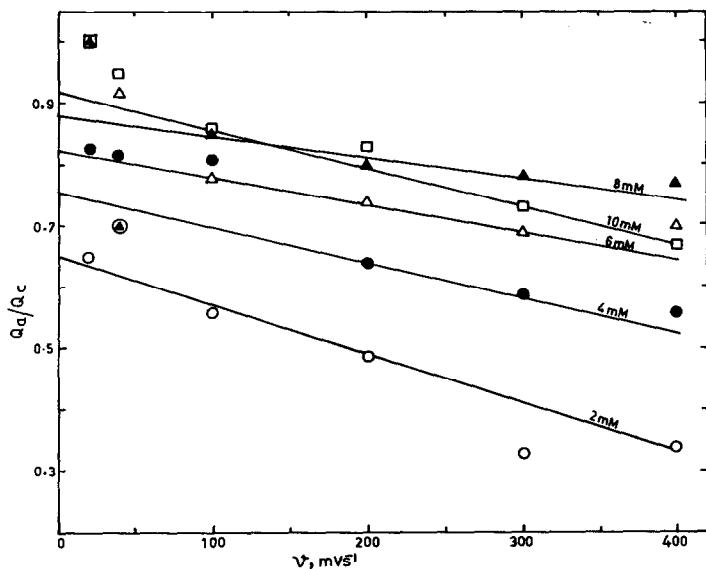
Fig. 6. Q_a/Q_c vs. scan rate for different concentrations of p-benzoquinone.
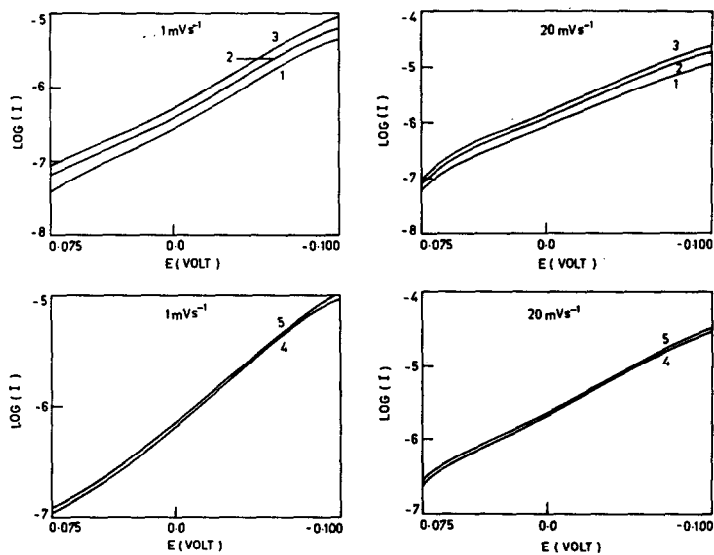

Fig. 7. Cathodic Tafel plots for different concentrations of p-benzoquinone: (1) 2; (2) 4; (3) 6; (4) 8, and (5) 10 mM.

ratio, especially at low range of sweep rates. The best reversibility of the reported system is, therefore, exhibited using an 8 mM concentration of p-benzoquinone in view of the fact that the relationships of both ΔE_p and Q_a/Q_c with scan rate are found to be in agreement and also the exchange current density is optimally highest at this concentration.
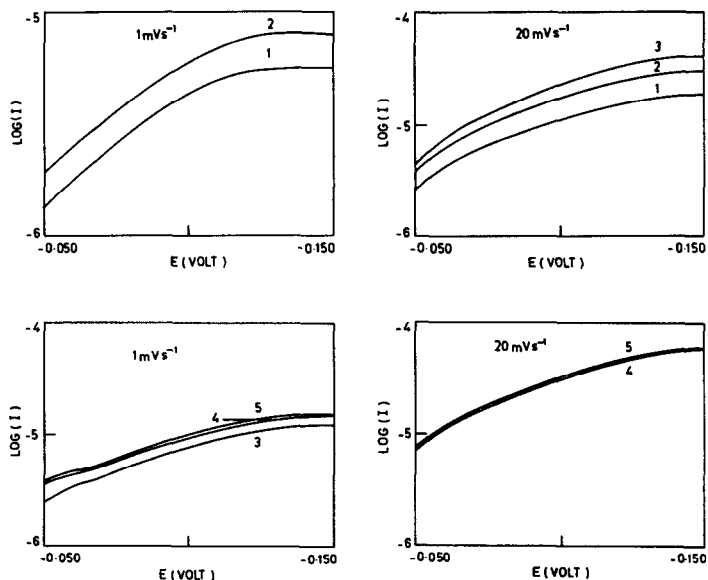
Fig. 8. Anodic Tafel plots for different concentrations of p-benzoquinone: (1) 2; (2) 4; (3) 6; (4) 8, and (5) 10 mM.

TABLE 3

Data on exchange current density, i_0 (mA cm^{-2}) obtained from Tafel plots

p-Benzoquinone concentration (mM)	Cathodic Sweep rate (mV s^{-1})		Anodic Sweep rate (mV s^{-1})	
	1	20	1	20
2	3.49×10^{-7}	8.50×10^{-7}	1.05×10^{-6}	2.29×10^{-6}
4	5.51×10^{-7}	1.02×10^{-6}	1.76×10^{-6}	2.58×10^{-6}
6	7.10×10^{-7}	1.26×10^{-6}	2.14×10^{-6}	2.72×10^{-6}
8	1.07×10^{-6}	2.23×10^{-6}	3.88×10^{-6}	5.45×10^{-6}
10	1.10×10^{-6}	2.32×10^{-6}	4.04×10^{-6}	5.64×10^{-6}

Acknowledgements

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