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ROOM TEMPERATURE ETHYL FORMATE FUEL CELLS FOR CONSUMER ELECTRONICS

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Abstract

There is a need to improve the energy and power density of power sources for consumer electronics. This paper describes some preliminary results on a room temperature fuel cell which can be refuelled by injection of fresh ethyl formate into the cell and the projected energy density is in the region of 60-100 Wh/kg, significantly better than the presently available rechargeable batteries.

1. Introduction

The continued growth in portable consumer electronic products has led to an ever increasing demand for higher energy and power density rechargeable batteries, culminating in the recent commercialisation of rechargeable Ni-Metal hydride batteries which have energy density of over 50 Wh/kg, significantly better than the traditional Ni-Cd batteries which give ~30 Wh/kg. However, there is a strong demand for even higher density batteries as to keep pace with the rapid micro-miniaturisation of electronic products. In addition, the need to recharge the batteries over a relatively long period of time is inconvenient. On the other hand, if fuel cells can be developed for such applications, there are many significant advantages:

- a) *High energy and power density—only fuel is consumed and air is used as the oxidant.*
- b) *Rapid recharging—it merely involves replenishing of the fuel.*
- c) *Low cost—provided the precious metal catalysts loading is not too high.*

However, the only fuel cell which can be operated at room temperature at present is the H₂-air fuel cell. Such cells are difficult to use in low wattage consumer electronics applications:

- a) *Hydrogen storage in mini-cylinders is expensive and relatively heavy.*
- c) *The operating voltage of a room temperature fuel cell is relatively low (0.6–0.7V) and though it is possible connect cells in series to achieve higher operating voltage, there is a need to ensure adequately spaced air channels between the cells and mechanical means to ensure adequate supply of air, which would reduce the volumetric energy density.*

However, if liquid hydrocarbon fuels can be used instead of hydrogen for room temperature fuel cell applications, it would have many advantages: light weight containers, inexpensive and easy to carry, analogous to lighter fluids.

Work by Tseung et al [1-4] has shown that co-electrodeposited Pt/WO₃ is a very active anodic electrocatalysts for the oxidation of methanol in acidic media, 60° C. This study has now been extended to the oxidation of formic acid at room temperature with surprisingly good results: 50mA/cm², 100 mV vs saturated calomel electrode (SCE). The electrode was a co-electrodeposited Pt/WO₃ on one side of a 1 cm² gold foil (Pt/WO₃ ~1/1, Pt loading 1 mg/cm²). There was no change in performance over a test period of 180 hrs. Preliminary estimates suggest that with further improvement in electrocatalyst composition and electrode structure, two formic acid fuel cells constructed as a bi-cell should give up to 1.0V at 100 mA/cm²! In addition, a recent Finnish invention [5] has shown that using a mosfet control unit, it is possible to increase the voltage of an electrochemical power source from 0.7V to 12V at an efficiency of 80-90%. However, formic acid presents some potential hazards during refilling and transportation and may not be acceptable as a fuel for consumer applications, even if stringent safety designs are incorporated to the system. Therefore, the ideal fuel should be safe and not be acidic. In other words, in the event of spillage during refuelling or accidental breakage of the container, it should not have a harmful effect. Some preliminary studies have shown that ethyl formate is a promising fuel for this application, since it is not a corrosive chemical. Methyl formate was judged to be unsuitable because of its low boiling point (35°C). When ethyl formate is injected into a fuel cell containing 0.5M H₂SO₄, it is catalysed by acid to form a mixture of formic acid and alcohol, both of which can be used as fuel. Therefore, these two recent breakthroughs paved the way for the development of room temperature ethyl formate fuel cells for powering consumer electronic devices, such as portable computers, camcorders and mobile phones etc and could possibly open the first applications of fuel cell technology on a world wide commercial scale.

2. Theoretical considerations

The overall anodic oxidation of formic acid is:



The complimentary cathodic oxygen reduction is:



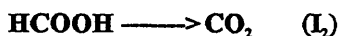
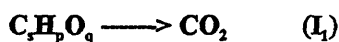
Hence the reaction in a formic acid fuel cell is:



The theoretical open circuit of the cell is ~1.2V. It is important to note that the use of formic acid both as the fuel and as the electrolyte have certain distinct advantages. Since no other acid anions are required, it is possible to use the changes in ionic conductivity or density as an indication of the amount of formic acid in the cell

(state of charge indication). In addition, since apart from formic acid, no other species in the electrolyte is consumed, replenishment of additional formic acid is a very simple and rapid procedure, possibly via a syringe injection of formic acid to the cell until the conductivity or density of the electrolyte reaches the desired value.

In practice, the anodic oxidation of formic acid on a Pt electrode involves many steps [6-9] and follows two different pathways:



where $C_rH_pO_q$ is a side product [10]. The partial current of I_3 is much larger than $(I_1 + I_2)$ under steady-state conditions in the Tafel region. The following reaction mechanism has been proposed for the CO_2 production by path 3: (I_3)



As yet, the existence of weakly bonded species is not confirmed experimentally, but regardless of whether these are ads or weakly bonded, it is clear that (3) and (4) will only occur on Pt sites which are free of $C_rH_pO_q$ and H_{ads} . The best performance recorded on platinised Pt is $5\text{mA}/\text{cm}^2$ at 370mV vs RHE in $1\text{M HCOOH} + 0.5\text{M H}_2\text{SO}_4$ ($\sim 1/10$ of the performance the recent Essex results) and that the rate determining step is (4) [9].

3. Some preliminary results on the oxidation of formic acid and ethyl formate on co-electrodeposited Pt/WO₃

Fig.1 shows the steady state performance of Pt/WO₃ electrode for the oxidation of formic acid and methanol at room temperature, indicating that formic acid is more readily oxidised. This is not surprising, since the oxidation of methanol involves many partial oxidation steps: methanol \rightarrow formaldehyde \rightarrow formic acid \rightarrow CO \rightarrow CO₂. Since formic acid is further down in the oxidation chain, its higher reactivity is no surprising. In addition, the performance is far more stable. Fig.2 shows the steady state performance in different concentrations of formic acid. $0.2\text{M Na}_2\text{SO}_4$ is added as the supporting electrolyte. An interesting point to note is that the performance in 1M and 5M formic acid is more or less similar after 30 min. On the other hand, the performance in 10M formic acid actually decrease, indicating that the performance is not controlled by the concentration of formic acid. At 60°C , the performance improved significantly $\sim 20\text{mV}$ vs SCE, $50\text{mA}/\text{cm}^2$. The performance in $5\text{M HCOOH}/0.2\text{M Na}_2\text{SO}_4$ remains unchanged over a test period of 175 hrs at room temperature and there is considerable improvement at 40°C . The ethyl formate concentration in $0.5\text{M H}_2\text{SO}_4$ was $11\text{ wt}\%$. initially. The electrode was a co-electrodeposited Pt/WO₃ plated on both sides of a 1cm^2 gold foil ($\sim 1\text{mg Pt}/1\text{mg WO}_3$). Though the performance is lower than those obtained for formic acid oxidation, it is still quite satisfactory. The lower performance is probably due to the low concentration of formic acid in the solution and the need to oxidise the ethanol in the solution. We have chosen to limit concentration of ethyl formate in sulphuric acid to $11\text{ wt}\%$ because this is the reported solubility limit of ethyl formate in water. However, since ethyl formate is catalysed by acid to form formic acid and ethanol, the solubility should be a lot higher. This is indeed the case (Fig.3). In practice, a ethyl formate will operate between $30\text{-}40^\circ\text{C}$ because of the unavoidable inefficiency in the system and the performance will also be improved with higher ethyl formate concentrations.

4. Discussion

As stated earlier, reactions (3) and (4) will only occur on sites which are free of H_{ads} and $C_rH_pO_q$ and it has been suggested that (4) is the rate limiting step. Therefore, by speeding up the oxidation of H_{ads} and $C_rH_pO_q$, it

should be possible to speed up (4). Co-electrodeposited Pt/WO₃ is ideally suitable for this purpose because of two unique properties:

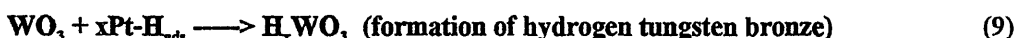
A) 'Hydrogen spill-over' effect

This was first experimentally verified by Hobbs and Tseung [11-12]. Basically, the oxidation of H₂ on Pt in acidic solutions involves:



where (8) is the rate determining step.

On the other hand, the anodic oxidation of H₂ on Pt/WO₃ in sulphuric acid media involves [11-12]:



where $x=0.33$. H_xWO₃ is blue in colour and electrically conducting. In this way, the surface reaction and the desorption reaction involving H_{ads} will be carried out on surfaces other than Pt, freeing the Pt site for other catalytic reactions. The room temperature anodic performance for a Teflon bonded H₂ based on 0.1mg Pt/10 mg WO₃/cm² is 400 mA/cm² at 40mV vs Dynamic Hydrogen Electrode (DHE), compared to only 250 mA/cm² for a 0.3mg Pt/10 mg TaC/cm² at 650mV vs DHE, confirming that WO₃ is indeed an active support.

B) Rapid surface reaction between CO_{ads} and OH_{ads} at the Pt/WO₃ interface

Niedrach and Weinstock [13] found that Teflon bonded containing mechanical mixtures of Pt black and WO₃ was far more resistant to poisoning to a impure stream of H₂ containing 2% of CO, compared to Pt black electrodes. They attributed their success to the fact that the CO_{ads} on the Pt surfaces reacts readily with the OH_{ads} on adjacent WO₃ sites:



Similar mechanism might be at work for the rapid oxidation of other organic intermediates adsorbed on Pt surfaces. This might also explain the seemingly anomalous effect in Fig.2, where the anodic activity is higher at lower formic acid concentration—the lower the acid concentration, the higher water activity, leading to greater available of OH_{ads}.

C) Uniform dispersion of Pt on WO₃ on an 'atomic' scale

The earlier work of Hobbs and Tseung relies on freeze drying of chloroplatinic acid on WO₃ powder. Whilst this ensures uniform dispersion of Pt particles around WO₃ particles, the present co-electrodeposition of Pt/WO₃ results in mixing of Pt and WO₃ on an 'atomic' scale, since scanning electron micrographs failed to reveal the presence of Pt particles and only transmission electron micrograph at x100000 and X ray line broadening studies showed that the Pt particles are less than 40Å and that the WO₃ phase is amorphous. The ability to disperse Pt in such a way significantly increases the amount of Pt/WO₃, leading to very high activity for formic acid oxidation even at low Pt loadings.

5. Development of prototype cells with DC-DC converter circuits to power portable electronic products

A typical rechargeable 6V, 1.5 A-hr rechargeable Ni-Cd battery for a camcorder weighs about 300g, i.e 30 Wh/kg. This does not take into account the weight and cost of the charger. Therefore, a prototype ethyl formate fuel cell should be able of give similar voltage (with a DC -DC converter built into the consumer electronic device) but at a very much higher energy density, ~60-100 Wh/kg. Since the operating potential of an ethyl formate fuel

cell is ~0.5V, it is difficult to envisage joining and refuelling 15 individual cells together in series to get the voltage up to 7.5V because of the common electrolyte effect and the need to have adequate volume for air channels. Preliminary studies at Essex and University of Hong Kong have indicated that the material and labour cost of building a DC-DC prototype in small quantities is £30, falling to £5 on volume production. Such a system should enable an ethyl formate bi-cell operating at 1V operating in conjunction with an appropriate DC-DC converter to satisfy the power requirements for most consumer electronic applications, provided the design criteria for ensuring no spillage under any operation conditions, rapid refilling etc are investigated in detail and evaluated.

6. Future work

Collaborative work between the Universities of Essex, Xiamen and Hong Kong in the next few years will be concentrated on the following remaining problems:

- Novel oxygen reduction catalysts which are less susceptible to the poisoning effect of ethyl formate on performance
- Improvement in the performance of the Pt/WO₃ anode
- Design, construction and evaluation of low cost, compact DC-DC converter
- Novel cell design to ensure safety and convenience of use
- Technical economic assessment of the ethyl formate cell for use in consumer electronics applications

Acknowledgements

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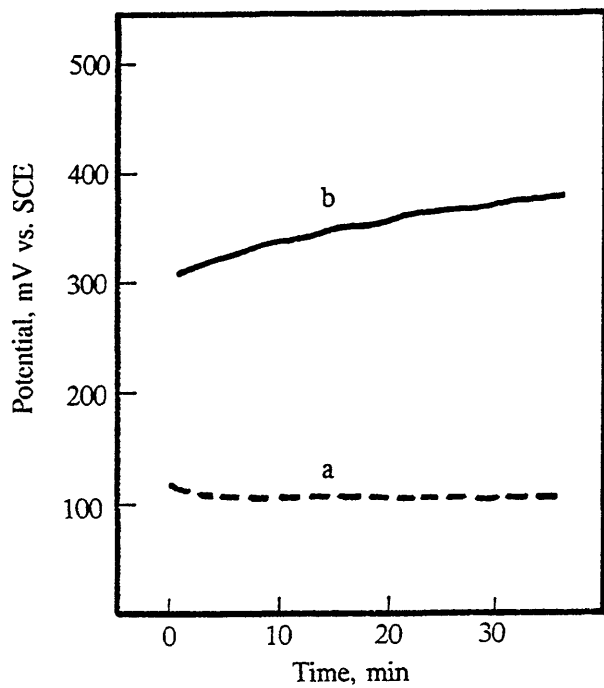


Fig.1 E - t curves of a Pt/WO₃ electrode at 50mA/cm² in (a) 5M HCOOH/0.2M Na₂SO₄ and (b) 5M CH₃OH/0.2M Na₂SO₄, 20°C.

Fig.2 E - t curves of a Pt/WO₃ electrode at 50mA/cm² in 0.2M Na₂SO₄ solution containing (a) 1M, (b) 5M and (c) 10M HCOOH. 20°C.

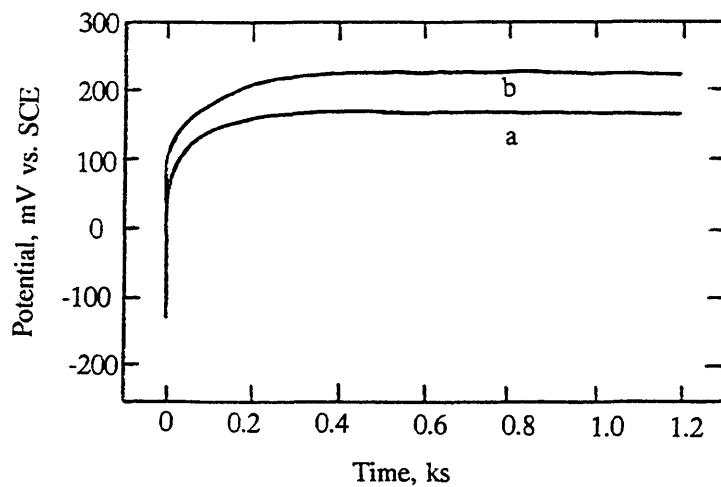
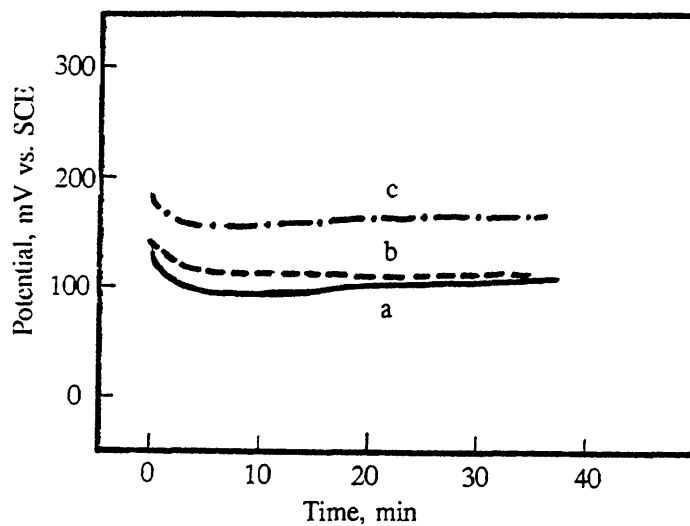


Fig.3 E - t curves of a Pt/WO₃ electrode at 50mA/cm² in 2M HCO₂C₂H₅/0.5M Na₂SO₄ solution at (a)40°C, (b) 20°C.