JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 137–141

# *A study of electrolyte-phobic molten carbonate fuel cell electrodes*

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Received 28 September 1971

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The incorporation of electrolyte-phobic material into gas diffusion electrodes enhances their performance. The principles governing the choice of electrolyte-phobic materials in molten carbonate electrolyte are discussed. Contact angle measurements of molten $NaLiCO_3$ on materials which have hexagonal layer-like structures confirmed that provided $\gamma_{LV} > \gamma_{SV}$, the contact angle will be greater than 90°. Of the materials tested (C, BN, $BaO.6.Fe_2O_3$, $PbO.6Fe_2O_3$), only C possessed adequate corrosion resistance. Electrolyte-phobic anodes, prepared by incorporation of graphite fibres into the electrocatalyst mixture, significantly reduced concentration polarization and paste electrolyte cells using such electrodes gave 160 mA/cm$^2$ at 0·6 V on 80% $H_2$/20% $CO_2$ fuel at 600°C, as opposed to 80 mA/cm$^2$ for conventional cells.

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## Introduction

Molten carbonate fuel cells based on $NaLiCO_3$ paste electrolytes use cheap reformed hydrocarbon fuels and inexpensive materials of construction [1]. However, despite the use of high operation temperatures (600–700°C), their performance is low, rarely exceeding 60–80 mW/cm$^2$. Though activation polarization is reduced by the increased temperature of operation, it is difficult to use high surface area electrocatalysts to improve the performance since they tend to sinter readily. Even if they are stabilized by the addition of sintering inhibitors [2], it is not possible to obtain greatly improved performance, since the electrodes will be flooded if the pores in the electrode are smaller than the pores of the inert MgO fillers (1–3 $\mu$) used in the paste electrolytes [3]. Moreover, paste electrolytes are difficult to fabricate. On the other hand, the use of dual porosity electrodes and free $NaLiCO_3$ electrolytes is not promising either since $NaLiCO_3$ has a very high surface tension (230 dynes/cm), compared to only 80 dynes/cm for KOH. Thus, very much higher gas pressures are required to maintain a comparable three-phase area in a dual porosity electrode operating in molten $NaLiCO_3$ electrolytes. Such electrodes are normally too weak to withstand high gas pressures at elevated temperatures. Present-day low temperature aqueous electrolyte fuel cells owe their greatly improved performance to the use of Teflon bonded electrodes [4]. These electrodes consist of two porous phases criss-crossing each other—the hydrophilic electrocatalysts structure is filled with electrolyte whilst the hydrophobic porous Teflon structure is kept dry, thus allowing rapid gas diffusion. Provided the aggregate size of the electrocatalyst is kept small [5], concentration polarization can be greatly reduced and almost all the electrocatalyst surface can participate in the electrochemical reaction. However, this concept has not been extended to molten carbonate fuel cell electrodes. Therefore, it is of interest to investigate materials which are not wetted by molten $NaLiCO_3$.

## Theoretical considerations

Fig. 1 shows the equilibrium shape of a drop of liquid resting on a solid surface. The contact

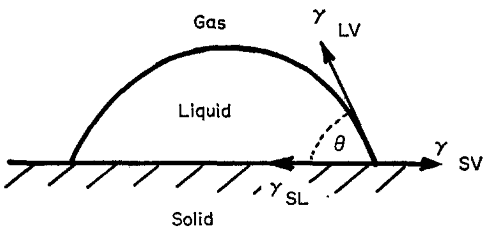

Fig. 1. The equilibrium contact angle at a solid–liquid–gas interface.
$\theta$ = contact angle
$\gamma_{LV}$ = interfacial energy between liquid and vapour
$\gamma_{SV}$ = interfacial energy between solid and vapour
$\gamma_{SL}$ = interfacial energy between solid and liquid

angle can be computed by the use of Young's equation [6]:

$$\gamma_{SV}-\gamma_{SL} = \gamma_{LV}\cos\theta \quad (1)$$

If $\theta$ is less than 90°, the liquid wets the solid. If $\theta = 0$, complete wetting occurs and the liquid spreads freely over the solid surface at a rate depending on the liquid viscosity and surface roughness. On the other hand, when $\theta$ is greater than 90°, no wetting occurs.

Thus if wetting occurs, the value of $\cos\theta$ will be positive; rearranging (1) and introducing the term $S_{LS}$, the spreading coefficient, into the equation, we have

$$S_{LS} = \gamma_{SV}-(\gamma_{LV}+\gamma_{SL}) \quad (2)$$

Thus, for wetting not to occur, it is necessary that $S_{LS}$ be negative. Thermodynamically, the most stable state of any system is that which results in the lowest free energy. Thus whether a liquid wets a solid is dependent on whether the total surface energy of the system will be decreased. Therefore, if $\gamma_{LV}>\gamma_{SV}$, then $S_{LS}$ will definitely be negative and no wetting occurs, i.e. $\theta>90°$. This prediction will be valid provided there is no chemical reaction between the liquid and the solid. The surface free energy of $NaLiCO_3$ is 230 erg/cm$^2$ at 600°C [1]. An examination of the surface free energy of the common metals and oxides [7] revealed that their values are very much higher than 230 erg/cm$^2$. On the other hand, the surface free energy value for a graphite single crystal is only 119 erg/cm$^2$ at room temperature [8]. The carbon atoms in graphite crystal are strongly held together by covalent bonds in the hexagonal basal plane but the bonds between the layers are weak Van der Waal bonds. Thus, a small amount of energy is sufficient to bring about an increase in surface area of graphite since the hexagonal arrays could easily be moved by rupturing the weak bonds. Similarly, BN, which also possess similar crystal structure [9], should have low surface energy. Though these compounds may be suitable for use in the anode, they will be readily oxidized at the cathode. Thus likely candidate materials for use in the cathode will be oxides possessing layer-like hexagonal structures. The hexagonal ferrites [10], $BaO.6Fe_2O_3$ and $PbO.6Fe_2O_3$ therefore merit further investigation. The structure of the unit cell is built up of spinel blocks each of which consists of four horizontal planes containing four oxygen atoms with nine ferric ions distributed between these planes. Between the spinel blocks are intermediate planes each of which contains a barium or lead ion, three ferric ions and three oxygen ions. Therefore, slip will occur more readily between the planes cutting the '*c*' axis, analogous to the layer-like graphite or boron nitride. Though the above materials may satisfy the surface energy requirements, the corrosion resistance of these materials towards molten $NaLiCO_3$ may not be satisfactory.

## Experimental

### *Materials*

Since graphite single crystals are not readily available, pyrolytic graphite and vitreous carbon were obtained from Le Carbone Limited. Carbon and graphite felt were obtained from Morganite Limited. Hot pressed BN samples were purchased from Carborundum Limited.

$BaO.6Fe_2O_3$ was prepared by calcining the appropriate amount of Analar grade BaO and $Fe_2O_3$ at 950°C for 24 hr. Similarly, $PbO.6Fe_2O_3$ was formed by heating the appropriate Analar oxide mixtures at 850°C for 24 hr to avoid the volatilization of PbO. The resultant powder was ground in an agate mortar. X-ray powder diffraction confirmed that in both cases the appropriate hexa-ferrites had been formed and that no detectable lines of the constituent oxides were present in the powder diffraction photographs. The powders were pressed at 5 tsi in a 1 in steel die and sintered at 1000°C for 24 hr. The $BaO.6Fe_2O_3$ pellets had an average density of 3·71 g/cc, i.e. 69·5% dense, whilst the $PbO.6Fe_2O_3$ pellets were 4·53 g/cc, or 79·5% dense. Though the presence of porosity could influence the exact contact angle value, it was felt that the samples would be satisfactory for our initial experiments—to see whether they are wetted by molten $NaLiCO_3$.

### *Contact angle measurements*

Fig. 2 shows a schematic diagram of the experimental facility used for contact angle measurements. 4–5 mm $NaLiCO_3$ beads were prepared by pouring drops of molten $NaLiCO_3$ on to a stainless steel tray. A bead was placed on top of the sample before the start of the experiment. The temperature was raised gradually at the rate of 100°C/hr and held constant at 520°C for ½ hr (melting point of $NaLiCO_3$—514°C) before proceeding to higher temperatures. The sessile drop was photographed with a 35 mm camera fitted with a close-up lens.

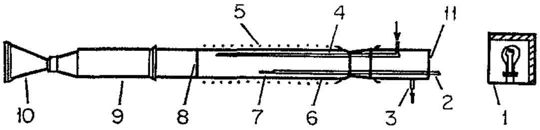

Fig. 2. Apparatus for measuring contact angle
1. Lamp; 2. Thermocouple sheath; 3. Gas outlet; 4. Gas inlet; 5. Heating tape; 6. Tube furnace; 7. Specimen support; 8 and 11. Ground glass windows; 9. Telescopic sight; 10. Camera

### *Electrochemical evaluation*

Materials which showed electrolyte-phobic behaviour were incorporated into actual molten carbonate fuel cell electrodes and tested either in a full cell or a floating half-cell assembly [1].

## Results and discussion

The contact angles of molten $NaLiCO_3$ on the various samples were measured from the sessile drop photographs and are tabulated in Table 1.

The results below showed that graphite and carbon materials are of definite interest. Though BN satisfied the structural requirements, it reacted with $NaLiCO_3$. It is surprising to see that when tested in air, $BaO.6Fe_2O_3$ was completely wetted by $NaLiCO_3$, whilst $PbO.6Fe_2O_3$ was electrolyte-phobic, despite the similarity in crystal structure. Though the X-ray diffraction failed to reveal the existence of unreacted oxides, it is still possible that there are some unreacted oxides present on the surface of the hexaferrites, since X-ray diffraction cannot normally detect the presence of a small percentage of impurities ($<5\%$). BaO, a high melting point oxide, is expected to be less reactive than PbO and there may be considerable amount of unreacted BaO and $Fe_2O_3$ present on the surface of the $BaO.6Fe_2O_3$. Under such conditions, the interfacial surface energy relationship will favour wetting. On the other hand, results for $PbO.6Fe_2O_3$ in air suggest that the amount of unreacted PbO and $Fe_2O_3$, if present on $PbO.6Fe_2O_3$, must be very small indeed. Unfortunately, when tested under $CO_2$, it was wetted by $NaLiCO_3$. It is possible that the existence of $CO_2$ accelerates the corrosion of $PbO.6Fe_2O_3$ because $PbCO_3$ could be formed from $PbO.6Fe_2O_3$, resulting in the formation of a ternary melt with $NaLiCO_3$. Some confirmation of this hypothesis is provided by the results for PbO in air and $CO_2$. The contact angle in air is higher than in $CO_2$ and it takes longer for complete wetting to occur.

Table 2 shows the performance of various paste electrolyte cells (electrolyte composition 63·5% MgO, 36·5% $NaLiCO_3$, 11·2 cm in diameter, 4 mm thick) using different anode catalysts compositions. Ag–ZnO powders, previously pre-sintered at 750°C for 24 hr, were used as cathode catalysts. The use of pre-sintered Ag–ZnO powder ensures that the cathode catalyst will not change its performance during the electrochemical evaluation. The cell assembly has been described in detail elsewhere [1].

Table 2 clearly indicates that the introduction of graphite fibres to the electrode has made it electrolyte-phobic (Cell B). Provided some $NaLiCO_3$ electrolyte is added to enable the porous Ni catalyst to be fully soaked with

*Table* 1. *Contact angle of molten $NaLiCO_3$ on different samples*

| *Material* | *Experimental condition* | *Contact angle* |
|---|---|---|
| Pyrolytic graphite | '*c*' axis parallel to horizontal plane, 600°C, 50% $H_2$/50% $CO_2$ | 150° |
| „ | '*a*' axis parallel to horizontal plane, 600°C, 50% $H_2$/50% $CO_2$ | 150° |
| Vitreous carbon | 600°C, 50% $H_2$/50% $CO_2$ | 98° |
| „ | 650°C, 50% $H_2$/50% $CO_2$ | 100° |
| „ | 700°C, 50% $H_2$/50% $CO_2$ | 103° |
| „ | 600°C, 100% $H_2$ | 103° |
| „ | 600°C, 100% $CO_2$ | 98° |
| Carbon felt | 600°C, 50% $H_2$/50% $CO_2$ | 101° |
| „ | 700°C, 50% $H_2$/50% $CO_2$ | 96° |
|  | 46 hr at 700°C, 50% $H_2$/50% $CO_2$ | 96° |
| Graphite felt | 600°C, 50% $H_2$/50% $CO_2$ | 109° |
| BN | 520°C, immediately after $NaLiCO_3$ bead has melted, 100% $H_2$ | 91° |
| „ | 575°C, 100% $H_2$ | 66° |
| „ | 600°C, 100% $H_2$ | 38° |
| „ | 6 min at 600°C, 100% $H_2$ | 28° |
| „ | 40 min at 600°C, 100% $H_2$ | 6° |
| $BaO.6Fe_2O_3$ | 520°C, immediately after melting of $NaLiCO_3$ bead, Air | 0° (melt penetrated into pellet) |
| $PbO.6Fe_2O_3$ | 600°C, Air | 98° |
|  | 24 hr at 600°C, Air | 97° |
|  | 600°C, $CO_2$ | 58° |
|  | 2 hr 600°C, $CO_2$ | 58° |
| PbO | 600°C, Air | 80° |
| „ | 4 hr at 600°C, Air | Complete wetting and signs of reaction |
| „ | 600°C, $CO_2$ | 52° |
| „ | 2 hr at 600°C, $CO_2$ | Complete wetting and signs of reaction. |

electrolyte, stable and high performance could be achieved (Cell C and Cell D).

In order to assess the performance of such electrolyte-phobic electrodes in greater detail, tests were done in a 'floating electrode' cell assembly using free $NaLiCO_3$ electrolytes as well. Fig. 3 confirms the results of the full cell tests and it is expected that the use of higher surface area Ni–Ag powder catalyst would lead to even better performance. Fig. 4 shows a photomicrograph of such an electrode which has been dipped into a molten $NaLiCO_3$ electrolyte and cooled to room temperature in

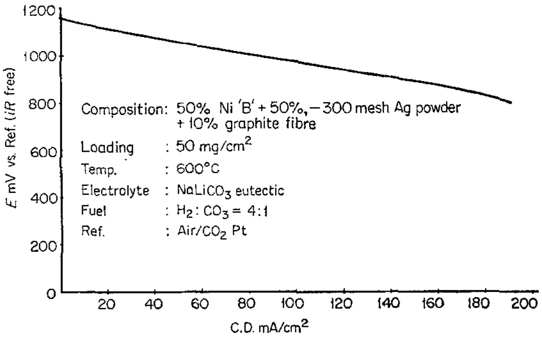

Fig. 3. Performance of electrolyte-phobic anode in free $NaLiCO_3$ electrolyte.

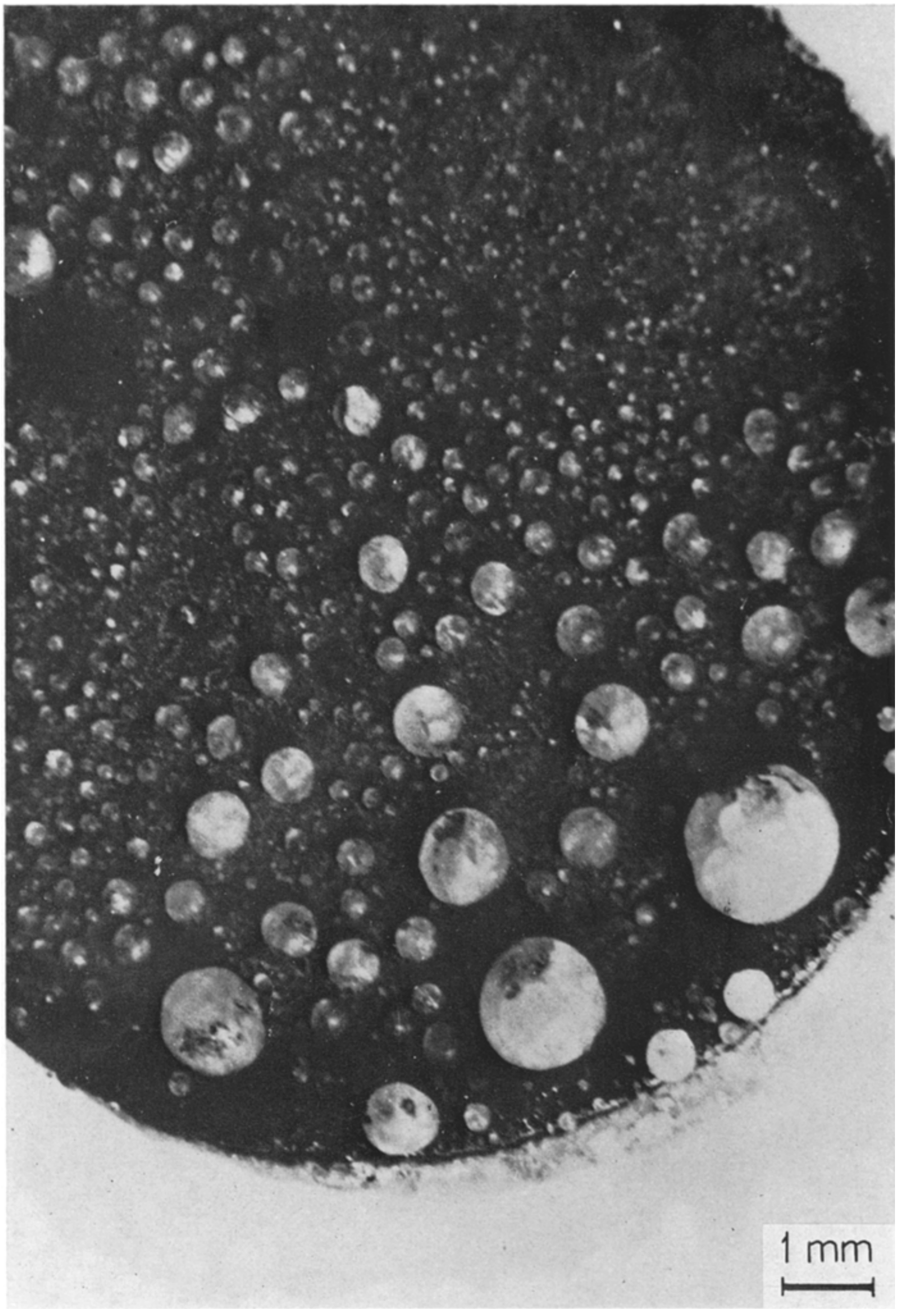

Fig. 4. Photograph of an electrolyte-phobic anode after complete immersion in $NaLiCO_3$ electrolyte at 600°C (×12 magnification).

*Table 2. Performance of various paste electrolyte cells*

Temperature of operation: 600°C
Fuel: 250 cm$^3$ $H_2$/60 cm$^3$ $CO_2$ per min.
Oxidant: Air + $CO_2$
Anode catalyst loading: 50 mg of catalyst/cm$^2$
Cathode catalyst loading: 50 mg of catalyst/cm$^2$

| *Designation* | *Anode material* | *Current density at 0·6 V* | *Comments* |
|---|---|---|---|
| 'Standard' cell | Ni 'B' powder | 80 mA/cm$^2$ | Performance stabilized at 60 mA/cm$^2$ after 24 hr |
| Cell A | 50% Ni 'B' and 50% of −300 mesh Ag powder | 125 mA/cm$^2$ | Slight signs of flooding |
| Cell B | Ni 'B' + 10% graphite fibre | 60 mA/cm$^2$ | Electrode easily lifted from paste electrolyte on conclusion of test, hardly wetted by electrolyte |
| Cell C | 50% Ni 'B' + 50% −300 mesh Ag powder + 10% graphite fibre + 10% $NaLiCO_3$ powder | 160 mA/cm$^2$ | Performance stable<br>No sign of flooding |
| Cell D | 50% Ni 'B' + 10% graphite fibre + 10% $NaLiCO_3$ | 160–180 mA/cm$^2$ | Performance stabilized at 120 mA/cm$^2$ after 24 hr |

$H_2/CO_2$. The solidified $NaLiCO_3$ electrolytes exist as small beads, distributed evenly on the electrode surface; this gave further confirmation that the electrode was indeed electrolyte-phobic.

## Conclusions

The incorporation of electrolyte-phobic graphite fibres into the molten carbonate fuel cell anode structure significantly improves its performance. This also allows the use of higher surface area electrocatalyst without danger of flooding. Unfortunately, attempts to find corrosion resistant electrolyte-phobic materials for use in the cathode were not successful.

## Acknowledgment

Part of this work was performed at Energy Conversion Limited. The author wishes to thank Energy Conversion and Partners for permission to publish; B. S. Harris of Energy Conversion Limited, and Miss A. Davidson of The City University for performing part of the experimental work.

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