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Short communication

Nanoporous H-sorbed carbon as anode of secondary cell

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ABSTRACT

Nanoporous carbon is proposed as reversible hydrogen electrode for an electrochemical cell operating in aqueous KOH solution. Hydrogen is stored by water electroreduction on the carbon electrode during the charging step, while nickel gauze is used as auxiliary positive electrode. Then, electrical energy is harvested by using the charged electrode as anode associated to an air cathode. A specific capacity of 390–450 Ah kg^{-1} of carbon material was measured. The system is technically more simple than a traditional fuel cell, since it does not require any hydrogen reservoir, membrane and noble metal for the hydrogen electrode.

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1. Introduction

Scarcity of fossil fuels and atmospheric pollution stimulate the research on advanced energy conversion systems. Lately, a great interest is devoted to fuel cells [1–3] which seem to be attractive energy sources. Among them, the Polymer-Electrolyte-Membrane Fuel Cell (PEMFC) is considered as one of the most promising power sources for vehicles as well as for portable electronic devices within the next decades. The PEMFC operates in aqueous solution at ca. 80 °C using oxygen from air and hydrogen [4] according to

$$H_2 + (1/2)O_2 \rightarrow H_2O \quad (1)$$

The cell generates electricity and heat, with water as only product, and is considered to be environment friendly. Unfortunately, serious drawbacks preclude a large scale development of this system. The main problems which remain to be solved are the following: (i) hydrogen has to be stored and transported in safe conditions and if possible at the lowest cost. Actually, none of the proposed solutions appears to be satisfactory, although some materials (metallic hydrides, nanoporous carbons, metal-organic frameworks) present interesting adsorption/absorption capacity values [5–8]; (ii) the only catalysts operating efficiently for di-hydrogen dissociation are noble and expensive metals such as platinum or its alloys. High catalyst loading on porous carbon supports must be used [9]; (iii) the anodic and cathodic compartments must be physically separated by a membrane permeable to the ions from the electrolyte, but not to gases. The efficient membranes available on the market are quite expensive [4,10]; (iv) the fuel cell produces water, which must be eliminated from the reaction medium by heating; (v) finally, the fact that the electrochemical process is irreversible (the cell cannot be recharged), might be a major disadvantage for an all-electrical based technology.

On the other hand, it is known that nanoporous carbon materials can reversibly store hydrogen by cathodic reduction of an aqueous solution at ambient conditions [11–13]. Hydrogen stored in carbon ⟨C⟩ by this process is weakly chemisorbed [14]; it will be further referred in the text to as carbon hydride, ⟨CH_x⟩. Due to this state of hydrogen, the carbon hydride is quite stable and could be used as anode in an electrochemical cell for producing electricity. Through this property of reversible hydrogen insertion in nanoporous carbons, we propose a novel concept of rechargeable cell, which allows the majority of the previously listed drawbacks of fuel cells to be circumvented. ⟨CH_x⟩ acts as a reversible anode charged using an auxiliary nickel electrode, whereas a diffusion air electrode plays the role of cathode during discharging.

2. Experimental

The cell is schematically represented in Fig. 1. It comprises three electrodes immersed in 6 mol L^{-1} KOH aqueous medium: a classical diffusion air electrode; the nanoporous ⟨CH_x⟩ reversible electrode; an auxiliary nickel electrode. The charging process of the cell is connected only with the hydrogen electrode, because the diffusion air electrode, consuming oxygen from air (so called breathing air electrode), does not need to be charged before operating.

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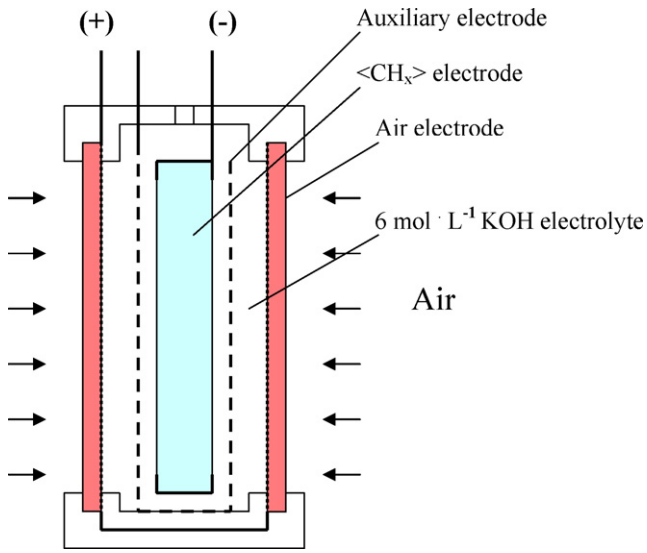

Fig. 1. Schematic representation of the rechargeable fuel cell based on a reversible carbon hydride ⟨CH_x⟩ electrode. The ⟨CH_x⟩ electrode is sandwiched between two parallel air electrodes. During the charging step, the carbon hydride is formed by cathodic reduction of water, using a nickel auxiliary electrode. During discharging, the ⟨CH_x⟩ electrode (−) is electrically connected to the air electrode (+) through the load. The electrolyte is an aqueous 6 mol L^{-1} KOH solution.

The material for the ⟨CH_x⟩ electrode is a self-standing nanoporous carbon cloth ⟨C⟩ obtained industrially by carbon dioxide activation of a viscose carbon cloth at 1273 K. The nitrogen adsorption/desorption isotherm of ⟨C⟩ has been determined at 77 K using a Micromeritics ASAP 2010. Prior to sorption, ⟨C⟩ was outgassed at 623 K until the pressure reached 10^{-6} mbar. Due to diffusive problems for the N_2 molecules at 77 K, it is assumed that the isotherms covering the whole range of relative pressure P/P_0 from 0 to ~0.98 correspond to the adsorption in micropores larger than 0.7 nm and in mesopores [15]. The specific surface area was calculated from the N_2 isotherm by applying the BET equation. For a detailed estimation of porosity, the CO_2 adsorption isotherm was also determined at 273 K. At low relative pressure $P/P_0 < 0.1$, the isotherm is assumed to correspond to the adsorption in ultramicropores (<0.8 nm). The ultramicropore volume V_{DRCO_2} was calculated according to the Dubinin-Radushkevich and Stoeckli [16] equations.

In order to reduce the distance between the air and the carbon hydride electrode during the discharging step, the ⟨CH_x⟩ electrode is placed between two parallel diffusion air electrodes electrically connected and forming the cell walls (Fig. 1). Each air electrode is built from two activated carbon layers: (i) the inner layer has a hydrophilic character which facilitates the transportation of the hydroxyl ions formed during oxygen reduction into the bulk of the electrolyte, and further to the ⟨CH_x⟩ electrode, where they are used for water formation during electrochemical oxidation of hydrogen; (ii) the outer one with hydrophobic properties allows air to diffuse easily where reaction takes place and simultaneously protects against electrolyte leakage [3]. The hydrophilic layer of the air cathode contains additionally a catalyst which decreases the oxygen reduction overpotential, e.g., 1 wt% platinum black. The two air electrodes with a total surface area of 40 cm^2 are glued into an organic glass square frame.

The ⟨CH_x⟩ electrode was made of 4 layers of activated carbon cloth (total mass of carbon 1.8 g) pressed tightly in a metallic frame used as current collector. The auxiliary electrode is made from nickel gauze in order to reduce the overpotential of oxygen evolution. A perforated separator placed between the electrodes (air, auxiliary and hydrogen) prevents from any short circuit in the cell.

During charging the cell, the ⟨CH_x⟩ electrode is polarized negatively and the Ni auxiliary one positively using a BT2000 multichannel potentiostat/galvanostat, Arbin Instruments, USA. The potential of each electrode was monitored vs a Hg/HgO reference electrode (+0.098 V vs NHE). Charging of the ⟨CH_x⟩ electrode is performed with a current density from 0.05 to 5 A per gram of carbon material. For a good efficiency of the process, the charging time was adjusted beyond the value corresponding to the nominal capacity of carbon.

3. Results and discussion

The activated carbon cloth presents a type I nitrogen adsorption isotherm typical of an essentially microporous material. The value of the Dubinin-Raduskevitch volume measured by CO_2 adsorption at 273 K, $V_{DRCO_2} = 0.291\ cm^3\ g^{-1}$, indicates that ⟨C⟩ contains a noticeable amount of ultramicropores which are the most efficient for hydrogen sorption [17–19]. The nitrogen adsorption data at 77 K show also that ⟨C⟩ has a moderate amount of mesopores, $V_{meso} = 0.019\ cm^3\ g^{-1}$, serving as rapid mass transportation pathway for ions [17,20]. The hydrogen electrosorption performance of this material is well-documented in references [12–14].

The cell is charged by negative polarization of the carbon electrode ⟨C⟩ while nickel gauze is used as positive auxiliary electrode. The redox reaction at the ⟨C⟩ electrode during the charging process can be summarized in Eq. (2):

$$\langle C\rangle + xH_2O + xe^- \rightarrow \langle CH_x\rangle + xOH^- \quad (2)$$

Simultaneously, on the auxiliary electrode, the oxidation of OH^- ions proceeds with oxygen evolution to the atmosphere according to reaction (3):

$$xOH^- \rightarrow (x/2)H_2O + xe^- + (x/4)O_2 \quad (3)$$

During the discharge (energy utilization), ⟨CH_x⟩ is acting as anode (oxidation process) whereas the air electrode is cathode. The reactions at the ⟨CH_x⟩ anode and at the diffusion air cathode run in opposite direction of (2) and (3), respectively. To summarize, while harvesting energy, the total reaction in the cell is

$$\langle CH_x\rangle + (x/4)O_2 \rightarrow (x/2)H_2O + \langle C\rangle \quad (4)$$

Reaction (4) is quite comparable to (1) showing that during the discharge, this system works as a fuel cell, and water which was consumed during the electrolysis process is regenerated. The application of an auxiliary electrode is necessary because the diffusion air electrode is made from carbon materials. The oxygen evolution directly on a carbon counter electrode during charging would lead to its oxidation, and in turn, to its chemical and mechanical destruction which would limit the cell durability.

The galvanostatic charge/discharge characteristics of the cell are shown in Fig. 2. As a result of charging with a negative current, the potential value of the ⟨CH_x⟩ electrode decreases below −1.5 V vs Hg/HgO. Simultaneously, the cell voltage increases up to ca. 2.5 V and it remains almost constant until the end of charging (Fig. 2A). In practical exploitation conditions, the cell can be discharged immediately after charging. However, in order to determine the equilibrium parameters, the cell was allowed to stabilize at open circuit. After few hours, the potential of the loaded carbon electrode stabilizes at −1.4 V vs Hg/HgO and the cell voltage at 1.55 V. Such low value of potential for the fully charged ⟨CH_x⟩ electrode is determined by a weak chemical C–H bonding as proved in our previous work [14] where it has been shown that the activation energy for hydrogen desorption is of the order of 110 kJ mol^{-1}. The discharging curves of the hydrogen/air cell and of the individual electrodes show (Fig. 2B) that the voltage profile and the capacity of the cell are determined only by the hydrogen electrode. The average

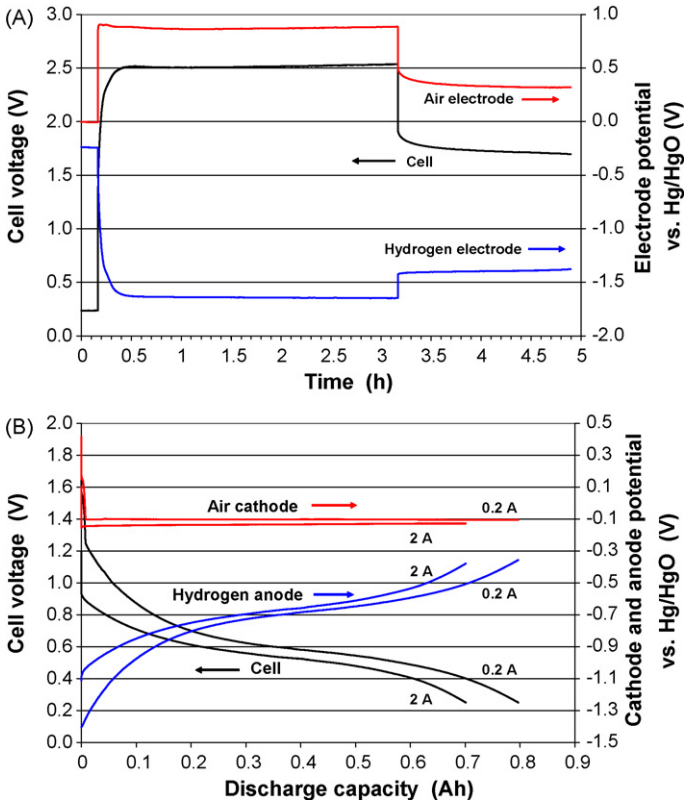

Fig. 2. Variation of the electrodes potential and cell voltage during galvanostatic charge/discharge of the cell: (A) charging with a current of 2 A between the porous carbon electrode and the auxiliary electrode during 3 h, followed by a relaxation period and (B) discharging of the ⟨CH_x⟩/air cell fully charged with currents of 0.2 or 2 A. Mass of ⟨C⟩ electrode: 1.8 g. Discharge current: 0.02 A.

value of cell voltage is ca. 0.6 V. The cell fully charged at 2 A is almost completely discharged after passing a current of 0.02 A during 35 h; it corresponds to a discharge capacity of 390 Ah kg^{-1}, i.e., 1.44 wt% of hydrogen. If the full charge is realized at 0.2 A during 90 h, the reversible capacity reaches 444 Ah kg^{-1} (1.65 wt% of hydrogen).

Fig. 3 shows the effect of the charging time at 2 A on the discharge capacity of the hydrogen electrode and of the cell. By comparing the shape of the curves, it is obvious that only the hydrogen electrode affects the cell performance. An increase of capacity is noticed when the charging time is changed from 1 to 3 h, but a further increase to 6 h does not improve the performance. Consequently, in order to keep a good efficiency (ratio between the discharge capacity and the charge capacity) of the process, the loading capacity of the cell

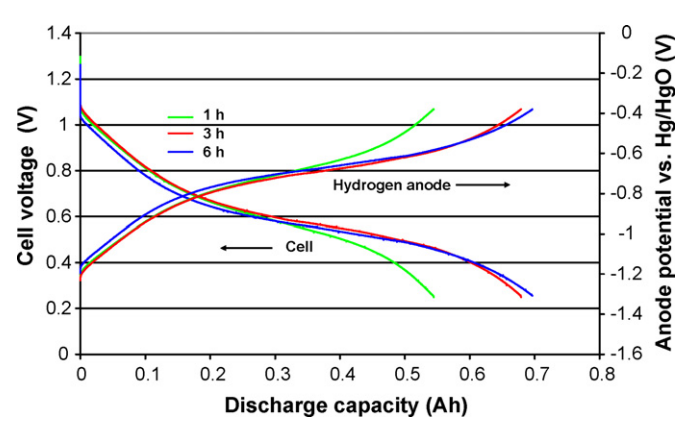

Fig. 3. Influence of the charging time on the discharging characteristics of the cell and of the hydrogen electrode. Charging current 2 A and discharging current 0.02 A.

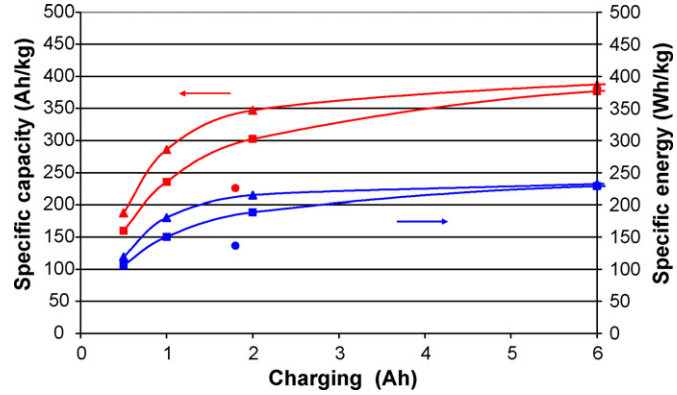

Fig. 4. Specific discharge capacity and energy (per mass of carbon electrode) of the ⟨CH_x⟩/air cell vs the charge passed at various values of charging current: (■) 2; (▲) 0.2; (●) 0.02 A. Discharging current: 0.02 A.

should not be higher than 2 Ah. Moreover, one can observe that a high charging capacity (12 Ah) leads to a performance aggravation, as demonstrated by a slightly smaller cell voltage.

In order to monitor the efficiency, the discharge capacity and energy density of the cell have been determined as a function of the charging capacity at different values of current, from 0.02 to 2 A (Fig. 4). Although the discharge capacity and energy density increase as the charging capacity increases, the best compromise in term of efficiency seems to be reached for charging current and capacity of 0.2 A and 2 Ah, respectively. The efficiency seems to be better with 0.2 A than 2 A, giving discharge capacities of 350 and 307 Ah kg^{-1}, respectively. On the other hand, a current of 0.02 A is not sufficient for reaching a suitable overpotential of water reduction, and in turn, the carbon electrode is not fully loaded with hydrogen.

The effect of the discharging current on the electrochemical characteristics is shown in Fig. 5. A current increase results in a decrease of cell discharge capacity and in a less marked plateau appearing at lower voltage. This slight reduction of performance is only due to the air electrode, which load is limited by diffusion processes [3]. The characteristics of the ⟨CH_x⟩ electrode itself are only very slightly affected by the discharge current.

In order to show the applicability of this new kind of cell, the cycle life has been investigated. The discharge characteristics of the cell during the 5th and the 15th cycles, for the same charge/discharge conditions, confirm a good cycling performance of the system (Fig. 6), without capacity fading. Moreover, we have already proved that the carbon electrode presents a good hydrogen reversibility over 100 cycles. All these properties demonstrate

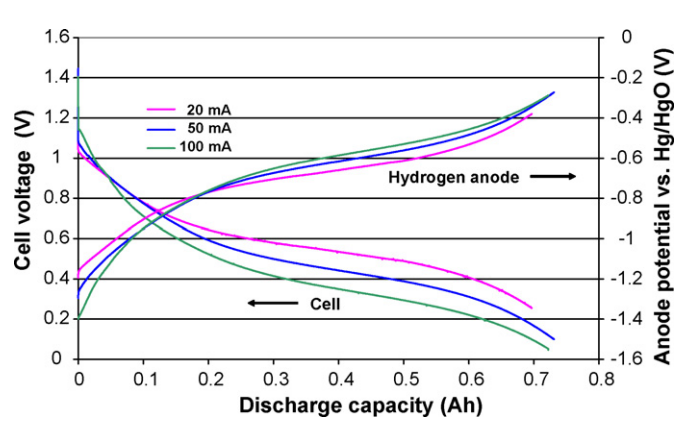

Fig. 5. Influence of the discharging current on the discharge characteristics of the cell and hydrogen electrode. Charging conditions: 2 A during 6 h.

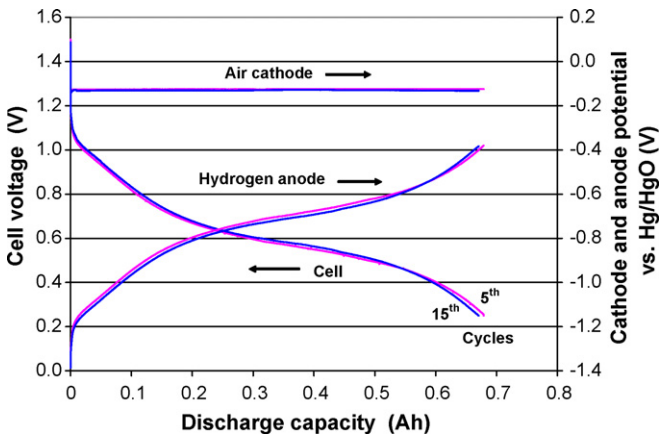

Fig. 6. Discharge characteristics of the cell during the 5th and 15th cycles. Charging conditions: 2 A during 6 h. Discharging current: 0.02 A.

that applications of this cell can be forecasted. Further optimization of the cell performance, e.g., for reaching a better defined plateau during discharge can be realized by selecting carbons with a more suitable hierarchical nanotexture [20,21].

4. Conclusion

This new concept of rechargeable cell presents several advantages. The hydrogen fuel is not supplied continuously, but is *in situ* produced and stored in the nanoporous carbon electrode during the charging process, and subsequently consumed by anodic oxidation. Neither a hydrogen reservoir, nor a semi-permeable membrane is requested. Since atomic hydrogen is inserted into carbon, a splitting noble metal catalyst is not required during discharging through anodic oxidation, being an important economical advantage. An additional profit of the proposed system is that water removal is not needed, whereas in conventional low temperature fuel cells, water produced through hydrogen oxidation by air must be removed at enhanced temperature. This cell can operate at room temperature, because water produced during the discharging process is electrochemically decomposed during charging. Taking into account the low cost of the materials which are used, the environment friendly nature of the electrolyte, this system is extremely promising for the portable electronic market.

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