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Evaluation of counter and reference electrodes for the investigation of Ca battery materials

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ABSTRACT

The growing needs for electrochemical storage systems are pushing the research community to explore alternatives to Li-ion technology. Ca-based chemistry is attracting more and more attention and expectation. However, the unsuitability of Ca metal as counter and reference electrodes limits the research activity on the topic. Herein we propose a simple electrochemical cell configuration employing activated carbon as counter and reference electrodes, which is suitable for positive electrode screening. The feasibility of this cell configuration has been confirmed by evaluating the electrochemical activity of bilayered-V_2O_5 in the Ca-ion system.

1. Introduction

The massive demand for batteries required by electromobility and stationary storage is pushing the research activity to evaluate electrochemical storage chemistries based on highly abundant elements, as alternatives to state-of-the-art Li-ion ones [1–3]. The use of more abundant and sustainable elements is expected to reduce the cost and the environmental impact of the battery. In particular, calcium, the fifth most abundant element in the Earth's crust also offering non-toxicity, low standard reduction potential (−2.87 vs. SHE), and high specific capacity (1340 mAh g^{-1}, 2060 mAh cm^{-3}), is an extremely appealing candidate for the realization of electrochemical storage devices [3]. However, the conditions to achieve efficient Ca stripping and deposition have not been found yet, due to the formation of passivation products at the Ca/electrolyte interphase, blocking any electrochemical reaction [4]. Although a limited number of electrolytes enabling the stripping deposition have been found [5–8], they are characterized by a rather limited efficiency, thus making the Ca metal unsuitable for counter and reference electrodes [9]. The resulting lack of a reliable cell configuration limits the possibility to test candidate positive electrode materials suitable for Ca^{2+} insertion, impeding the progress and research on the topic [10]. Here we propose an alternative cell configuration, employing activated carbon (AC) as a counter electrode and quasi reference electrode (QRE) as a reliable system for the electrochemical characterization of positive electrodes for Ca-ion batteries. The use of AC, which stores charge through the formation of double layers, as the counter electrode overcomes the issue associated with the unsuitability of the Ca metal, allowing to perform the screening of positive electrode materials candidates for this technology [10]. Moreover, AC generally operates within the electrochemical stability window of the electrolyte, thus avoiding the occurrence of electrolyte decomposition processes resulting in the formation of unwanted products, which may further affect the positive electrodes' performance. However, the use of AC as a counter electrode requires a three-electrode configuration with a reliable reference electrode, as the potential of the AC counter electrode varies depending on the amount of charge accumulated in the double layer. Thus, a stable reference electrode is needed to guarantee a precise control of the positive (working) electrode potential, which is critical for the mechanism study of electrode materials and, later, the design of full cells, e.g., calcium-ion batteries [10]. The use of the AC as a QRE has been demonstrated reliable in lithium cells [11], however, it has not be evaluated for calcium cells, so far. In this work, the suitable use of AC as QRE and counter electrode for calcium-based cells is verified enabling their use for the evaluation of positive hosts for Ca^{2+}.

2. Results and discussion

Fig. 1a reports the scheme of the three-electrode Swagelok cell used in this study. Free-standing AC electrodes are used as counter electrode and QRE. The use of a rather high areal loading of AC (generally ≥ 40 mg cm^{-2}

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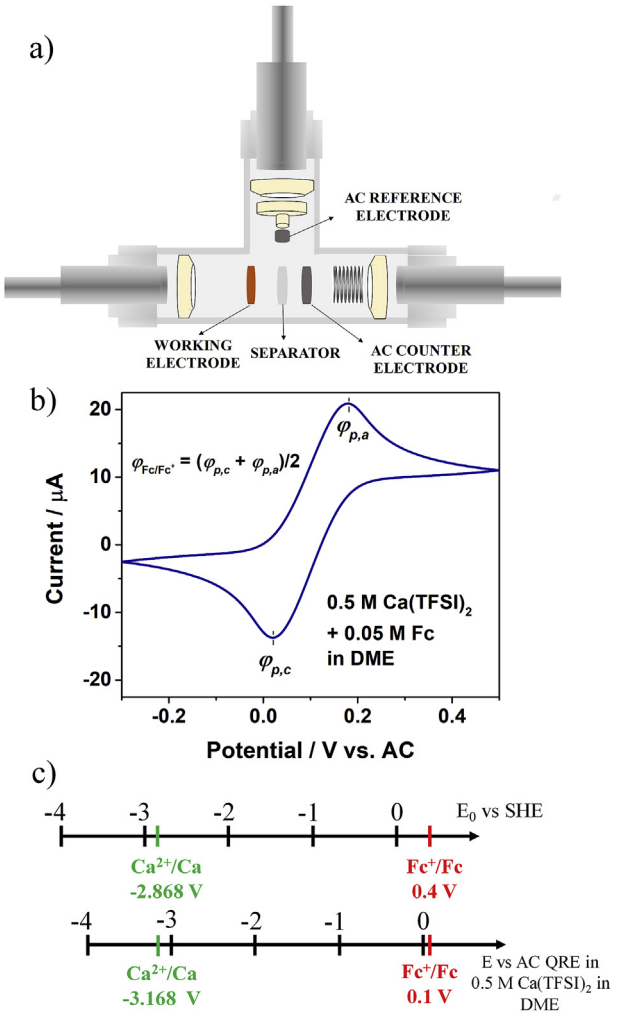

Fig. 1. (a) Scheme of the three-electrode Swagelok cell. (b) Cyclic voltammogram (CV) of 0.05 M Fc in 0.5 M Ca(TFSI)$_2$ in DME solution at 10 mV s^{-1} (WE: Au, CE: AC, QRE: AC). (c) Position of the Fc$^+$/Fc and the Ca^{2+}/Ca *vs.* SHE (upper) and AC QRE (lower).

corresponding to a capacity of 1.2 mAh cm^{-2}) for the counter electrodes guarantees the capacity to sustain the current density arising from the redox processes occurring at the working electrode (1.5 mg$_{V_2O_5}$ cm^{-2} corresponding to 0.4 mAh cm^{-2} assuming the maximum capacity to be 1 mol of Ca per mole of V_2O_5). The main advantage of using the AC counter electrode comes from the charge storage mechanism being purely capacitive without involving electrochemical reactions, thus avoids any electrolyte contamination by decomposition products [10]. Although these electrodes suffer from the variation of the salt concentration in the electrolyte upon charge and discharge [10,12,13], this issue can be easily overcome by using an excess electrolyte, which leads to negligible salt concentration variation. In this study, 450 µL of 0.5 M electrolytes employing Ca(TFSI)$_2$ salt were used. The capacity required for the electrochemical absorption of all the Ca^{2+} or $TFSI^-$ in the electrolyte by the AC counter electrode was calculated to be 1.2 mAh, while the capacity of the V_2O_5 electrode was generally ≤0.4 mAh. Therefore, in the performed test conditions, the maximum salt concentration change in the electrolyte was ≤3%. Eventually, higher positive electrode capacities can be easily compensated by increasing the electrolyte amount. This cell configuration can only be used for fundamental investigations regarding the Ca^{2+} storage mechanism in positive electrode materials, but not to estimate any energy performance.

To ascertain the feasibility of using AC as a quasi reference electrode (QRE), also, careful calibration and reliability tests were performed [11]. The calibration of AC QRE was performed using a standard redox reference system, i.e., the ferrocene/ferrocenium ion (Fc$^+$/Fc) redox couple [14], which potential *vs.* the standard hydrogen electrode (SHE) can be roughly assumed unaltered by the nature of the electrolyte. Thus, the Fc$^+$/Fc couple potential can be used to calibrate the AC QRE. Even more important, any drift observed for the Fc$^+$/Fc couple potential *vs.* AC QRE actually reflects the drift of the AC QRE potential [14]. Fig. 1b shows the cyclic voltammogram (CV) curve obtained for a three-electrode cell composed of 0.05 M Fc and 0.5 M Ca(TFSI)$_2$ in DME as the electrolyte, AC counter electrode, AC QRE, and gold working microelectrode. The potential of the Fc$^+$/Fc *vs.* the AC QRE was calculated using equation (1):

$$\varphi_{Fc/Fc^+} = \frac{\varphi_{p,c} + \varphi_{p,a}}{2} \quad (1)$$

where φ_{Fc/Fc^+} is the measured potential of the ferrocene/ferrocenium couple, $\varphi_{p,c}$ and $\varphi_{p,a}$ are the cathodic and anodic peak potentials, respectively. Fig. 1c compares the scale of the potential value of the Fc$^+$/Fc redox couple *vs.* SHE and *vs.* AC QRE. The Fc$^+$/Fc redox potential vs. AC QRE is 0.3 V lower than *vs.* SHE, which thus shifts all the potential values measured *vs.* AC of −0.3 V. Accordingly, the potential of the Ca^{2+}/Ca redox couple is expected at −3.168 V *vs.* AC QRE, as marked in the figure. It must be mentioned that the potential of the AC QRE *vs.* SHE could be different once the electrolyte composition and the activated carbon specifications change. A change of the electrolyte composition varies the ionic speciation in solution, which influences the charging phenomena at the AC/electrolyte interface [15]. Also, the nature of the AC material, in particular, the surface functionalization, can significantly influence the charging phenomena at the interface as well [16–18]. For these reasons, the above mentioned potential value of the AC QRE must be evaluated when the electrolyte or the AC material are changed. The stability of the AC QRE potential was evaluated by performing continuous CV and verifying eventual drift of the measured potential of Fc$^+$/Fc redox couple *vs.* AC QRE. Fig. 2a shows selected CV measurements performed on a three-electrode cell employing AC counter electrode, AC QRE, gold working electrode, and 0.05 M Fc + 0.5 M Ca(TFSI)$_2$ in the DME electrolyte. The measurement evidences an excellent overlapping of the measured curves, indicating a stable potential of the AC QRE. The measured potential of the Fc$^+$/Fc redox couple *vs.* AC QRE over time is reported in Fig. 2b for various electrolytes comprising the 0.05 M Fc + 0.5 M Ca(TFSI)$_2$ in different solvents, namely ACN, DME, EC:PC. The measurements demonstrate a significant influence of the solvent composition on the potential value and the stability of the AC QRE. In fact, for the electrolytes employing ACN or EC:PC as the solvents, the initial potential is 0.16 V *vs.* AC QRE, while for that employing DME is 0.10 V *vs.* AC QRE. The most relevant effect of the various solvents, however, is the AC QRE potential drift, which is −10.1, −7.7, and −0.9 mV/day for ACN, EC:PC, and DME based electrolytes, respectively. Several cells employing ACN- or EC:PC-based electrolytes were tested, always showing an excessive potential drift. Therefore, these tests were discontinued.

In pseudo-reference electrodes, the redox couple that defines thermodynamic equilibrium for electrons is not well-defined, so stable measurements depend on the electrode potential and bulk solution remaining unchanged during testing. The success of carbon pseudo-reference electrodes depends on a high surface area to limit the potential drift.

Generally, the potential drift is associated with the specific adsorption/de-adsorption of anions/cations on activated carbon, charging the electrode and leading to the potential drop at the electrode/electrolyte interface [15]. However, the systems here investigated contain the same ionic species at the same concentrations. Thus, we can speculate that the difference in the potential drift can be associated with the different ionic speciation in the electrolyte due to the ions/solvents interactions, which affects the surface adsorption and thus the electrode potential [11,19]. The higher donor number (DN) of DME, for example,

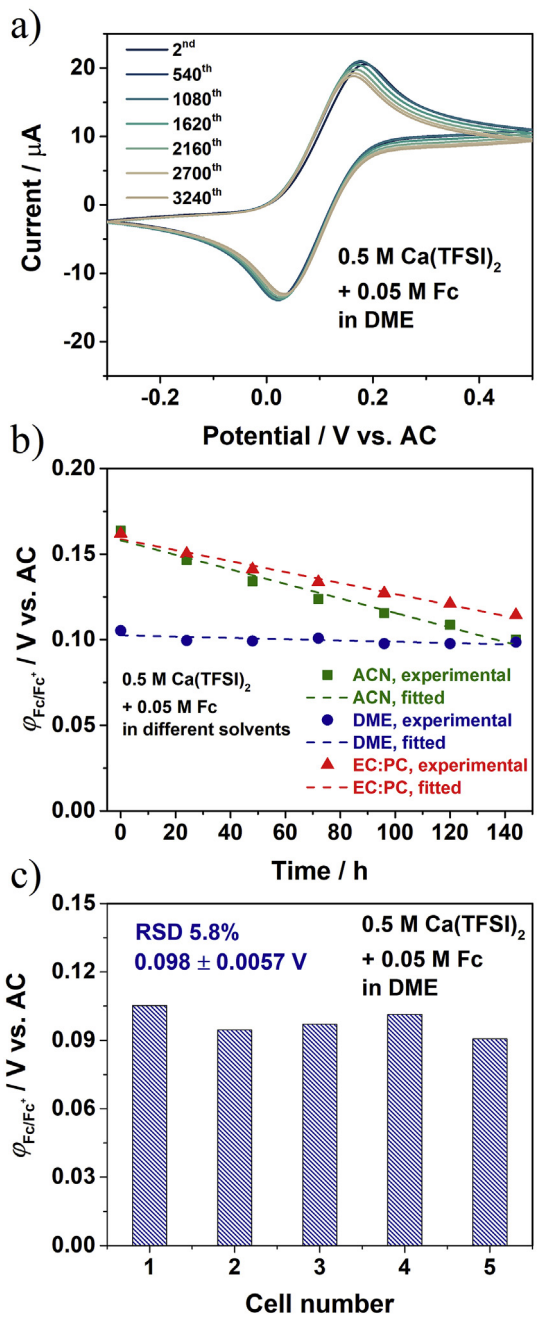

Fig. 2. (a) CVs at selected cycles in 0.05 M Fc + 0.5 M $Ca(TFSI)_2$ in DME at 10 mV s^{-1} against AC. (b) Evolutions of φ_{Fc/Fc^+} against AC in different electrolytes. (c) φ_{Fc/Fc^+} against AC in 0.05 M Fc + 0.5 M $Ca(TFSI)_2$ in DME of five reproduced cells after 24 h.

certainly results in the formation of more stable ion-solvent complexes, which may explain the higher stability of the AC QRE in DME-based electrolyte [20,21]. Moreover, the lower dielectric constant of the DME (7.40) with respect to the ACN (37.7) and EC (89.79)-PC (64.92) can lead to the formation of aggregate species in the electrolyte solution [22].

The obtained results demonstrate that AC QRE can be effectively employed in the DME-based electrolyte, while its use is not feasible in ACN and EC:PC based electrolytes, particularly for long-term measurements. The reproducibility of the potential measured employing the DME-based electrolyte has been verified testing five identical cells, which results are graphically depicted in Fig. 2c. The relative standard deviation as low as ± 5.7 mV proves that the potential measurement is reproducible for different cells, confirming the suitability of AC QRE in such an electrolyte [11].

The developed AC-based counter and quasi reference electrodes have been employed to investigate the electrochemical activity of bilayered-V_2O_5 as a host material for Ca^{2+} [23]. Fig. 3a shows the cycling behavior of the V_2O_5 electrode subjected to galvanostatic cycling at 20 mA g^{-1} within the potential window −2.0 - 1 V *vs.* AC QRE (i.e., 1.168–4.168 V *vs.* Ca^{2+}/Ca). The test evidences the electrochemical activity of the positive electrode material, showing an increase of the delivered capacity upon cycling. Fig. 3b reports selected voltage profiles recorded upon the cycling test. The evolution of the voltage profile shape upon cycling is characterized by a remarkable increase of plateaus associated with a reversible electrochemical process. In Fig. 3c, the corresponding differential profiles exhibit several redox peaks implying a multi-step electrochemical process for the (de-)intercalation of Ca^{2+} in V_2O_5. The possibility of Ca^{2+}-solvent co-insertion cannot be excluded from our results. However, previous investigation on Na^+-ion intercalation in V_2O_5 electrodes, also performed employing the glyme based electrolyte, excluded the [Na^+-solvent] co-intercalation occurs [23]. The overall

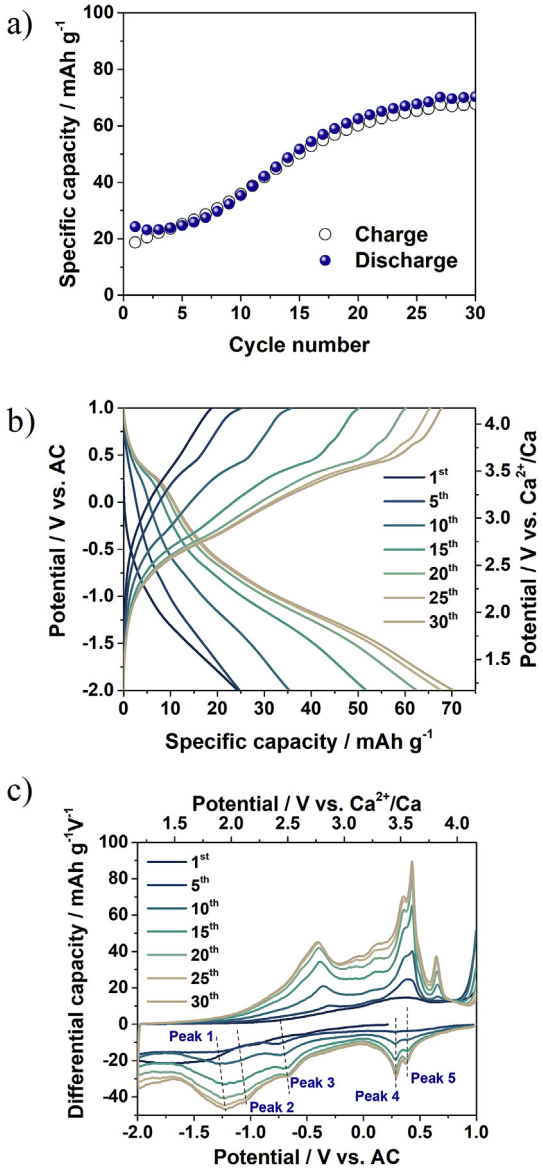

Fig. 3. (a) Specific capacity evolution of the bilayered-V_2O_5 electrode at a specific current of 20 mA g^{-1} within the potential window of −2.0–1 V vs. AC upon 30 cycles in 0.5 M $Ca(TFSI)_2$ in DME. (b) Charge-discharge and (c) corresponding differential profiles at selected cycles.

trend roughly resembles that occurring upon lithiation and de-lithiation of V_2O_5 [24–26], showings two peaks at high voltage, followed by a third broad feature at lower voltages. Although it is behind the scope of this short communication, it is interesting to notice the rather large number of features appearing, which is absent upon lithiation and deserves a more detailed investigation via in situ XRD and XAS. The increasing intensity of the peaks upon cycling corresponds to the observed increase in capacity upon cycling and indicates some sort of electrochemical induced activation processes. Regarding the herein proposed AC QRE, it can be observed that the peak potentials associated with the reversible electrochemical processes (peaks 4-5) do not drift during the measurements (around 150 h), confirming the suitability of such a pseudo-reference electrode in this specific cell. The shift of the peaks 1-3 can be, most likely, associated with the electrochemical activation process. All these results demonstrate the feasibility of our proposed cell configuration for positive electrode screening.

As mentioned above, the purpose of this short manuscript is the validation of AC as counter and reference electrodes in 0.5 M $Ca(TFSI)_2$ in DME electrolyte. Based on the results shown here, the origin of the electrochemical activity of V_2O_5 as the positive electrode in Ca-based batteries is presently performed in our laboratories.

3. Conclusions

An alternative electrochemical cell configuration employing AC as counter electrode and QRE, has been evaluated for Ca-ion positive electrode testing. The evaluation of the stability and reproducibility of the AC QRE evidenced the influence of the electrolyte composition, revealing that a careful assessment of the suitability of the system needs to be carried before the use. Nonetheless, the proposed cell configuration revealed good reproducibility and stability when employing the 0.5 M $Ca(TFSI)_2$ in DME electrolyte. The cell configuration has been successfully employed to perform the electrochemical characterization of bilayered V_2O_5 positive electrodes. The proposed system is a suitable solution for the screening of the electrochemical activity of positive electrode materials for Ca^{2+}-ion batteries.

4. Experimental section

Activated carbon (AC, YP-47, Kuraray), polytetrafluoroethylene dispersion (60 wt% in water, Sigma-Aldrich), carbon paper (TP-030T, Quintech), carbon black (C65, IMERYS), polyacrylic acid (PAA, average M_v of ~ 1,250,000, Sigma-Aldrich) were used as received. Molecular sieves (3 Å, Alfa Aesar) were dried at 300 °C under vacuum (10^{-3} mPa) for more than one week. Acetonitrile (ACN, VWR, anhydrous), ethylene carbonate (EC, BASF, battery grade), propylene carbonate (PC, BASF, battery grade), 1,2-dimethylglycol ether (DME, Sigma-Aldrich, 99.5%) were dried over the pre-dried molecular sieves for three days. The water content of the solvents after drying was lower than 10 ppm, as measured with Karl-Fischer Titrator. Ferrocene (Fc, Alfa Aesar, 99%) and calcium bis(trifluoromethanesulfonyl)imide ($Ca(TFSI)_2$, Solvionic, <50 ppm water, purity > 99.5%) were dried at 40 °C and 120 °C under vacuum (10^{-3} mPa) before use, respectively. This salt was selected because, to the best of our knowledge, is one of the few, if not the only one, available in anhydrous form and high purity. The 0.5 M solution of $Ca(TFSI)_2$ in DME as the electrolyte was chosen because a rather high salt electrolyte concentration is required to limit the effect of anion depletion of the AC counter electrode. On the other hand, the 0.5 M solution of $Ca(TFSI)_2$ in DME is rather close to the solubility limit.

Bilayered-V_2O_5 was prepared via a microwave-assisted hydrothermal method, which has been reported elsewhere [23].

The various electrolytes were prepared to dissolve proper amounts of $Ca(TFSI)_2$ in the various solvents in order to achieve 0.5 M solutions. Fc was added to the electrolyte to the 0.05 M concentration. The electrolyte preparation was carried out in an Ar-filled glovebox with H_2O and O_2 levels of <0.1 ppm. Freestanding AC electrodes were prepared according to the previously reported procedure [27]. The mass ratio of AC active material to PTFE binder was 8:2. Bilayered-V_2O_5 electrodes were fabricated in the dry room by doctor-blade casting on carbon paper slurries composed of 70 wt % active material, 20 wt % C65, and 10 wt % PAA in ethanol. Both AC and V_2O_5 electrodes were dried at 150 °C under vacuum (10^{-3} mPa) for 12 h. The average mass loading of V_2O_5 was 1.5 mg cm^{-2}. The average mass loading of AC was 40 mg cm^{-2}. The AC specific capacity is around 30 mAh g^{-1}. Thus, an electrode areal loading of 40 mg cm^{-2} corresponds to an areal capacity of 1.2 mAh cm^{-2}. For the V_2O_5 electrodes, a specific capacity of 270 mAh g^{-1} (about 1 mol of Ca per formula unit) is assumed. Thus, an areal loading of 1.5 mg cm^{-2} corresponds to an areal capacity of 0.4 mAh cm^{-2}.

The assembly of three-electrode Swagelok-type cells was also carried out in the Ar-filled glovebox (H_2O and O_2 levels below 0.1 ppm). The reference electrode validation tests were performed by cyclic voltammetry of three-electrode cells employing 12 mm and 8 mm free-standing AC electrodes as counter and reference electrodes, respectively. Au microelectrodes (0.79 mm^2) were used as working electrodes. 450 µL of electrolyte, i.e., 0.5 M $Ca(TFSI)_2$ and 0.05 M Fc solution in the various solvents, were added to each cell. Cyclic voltammograms at a scan rate of 10 mV s^{-1} were recorded using the VMP galvanostat/potentiostat (Bio-Logic, France). The electrochemical characterization of V_2O_5 positive electrodes (12 mm) upon Ca^{2+} insertion/extraction has been performed using 12 mm and 8 mm free-standing AC electrodes as counter and reference electrodes and 450 µL 0.5 M $Ca(TFSI)_2$ in DME as electrolyte. The galvanostatic cycling test with potential limitation (GCPL) was performed using the MACCOR series 4000 battery cycler and a specific current of 20 mA g^{-1} within a potential window of −2.0 - 1 V vs. AC QRE. Prior to any electrochemical measurement, the cells were stored for 12 h to reach a stable open circuit potential and a proper electrode wetting. All the electrochemical tests have been performed in climatic chambers set at 20 °C.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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